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Engineering Chemistry

B Sivasankar

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Preface

Engineering and technology have become inter-disciplinary with chemical, physical and biological sciences contributing immensely to the development of engineering practices. Applied chemistry is a fascinating area with profound implications for engineers as well as biologists. Materials fabricated and used in our daily life are obviously derived from chemicals, both natural and synthetic and their range of utility are growing day by day. It is imperative that engineers of different disciplines acquire sufficient knowledge of the materials and their characteristics for making proper selection of their end use applications. The use of tailor made materials of specific end uses have almost become the order of day. Fine tuning the properties of materials through the development of necessary chemical processes are in the realm of practicing chemists but it is the job of practicing engineers to define the basic requirements of specific end uses and to evaluate the finished products for stated purposes. Hence, a basic understanding of the chemistry of materials and processes is a must for an engineer or a technologist. A proper perspective of applied chemistry requires a sound knowledge of the underlying principles. The present book envisages at providing the necessary introduction of the chemical principles involved and applications of various materials and devices in a comprehensive manner yet understandable to the students aspiring to become practicing engineers.

Objective

The book has been prepared to cater to the needs of engineering students with sufficient background of chemistry acquired at the Senior Secondary level. The objective is to present the necessary theoretical aspects required for understanding intricacies of the subject and also give sufficient exposure to the applied chemistry aspects in different disciplines of engineering. Universities in India have prescribed syllabi with varying emphasis on diverse topics of interest to engineers. The depth of coverage of each topic varies, with some syllabi oriented towards applied aspects, while others stressing more on characterisation, particularly with instruments. The present book has been prepared taking into account the requirements of engineering students of different Universities, giving an in-depth coverage of a wide range of topics and hence will be useful for engineering & technology students and also to teachers in preparing for their lectures.

Organisation

The presentation as well as treatment of topics are user friendly and would make the reader comfortable while going through the book. The first few chapters deal more with the fundamental aspects such as thermodynamics, chemical kinetics, solid state, electrochemistry and phase equilibria as well as applications of relevance. Two chapters have been presented exclusively on analytical chemistry involving the classical and instrumental methods to make engineers feel at ease and also give them an insight with regard to the use of different methods by chemists for characterising materials. The last few chapters deal with application oriented topics of relevance to engineers and technologists.

Features

This book on Engineering Chemistry is written with the intention of discussing the required topics at the right level keeping in mind the practical applications of the subject in the field of engineering. It offers an exhaustive coverage of the topics (especially the applications) and lucid explanation of concepts as per the present day needs and practices.

- The book follows an application based approach. There is a perfect link between theoretical aspects and relevant applications.
- Theory and fundamental aspects are discussed in the first 6 chapters followed by application oriented topics with appropriate theory in the later chapters. Coherent organisation of the main topics followed by a logical progression of subtopics make the subject easy to understand.
- A methodical approach has been followed while dealing with the conceptual and theoretical aspects of all topics.
- For more clarity, tables and figures are interspersed throughout the book.
- To enhance comprehension, solved examples have been included in many chapters.
- Review questions enable recall of concepts explained in each chapter.
- Important topics such as Photochemistry in Natural Systems and Industries (Chapter 6), Pollutions of Environment (Chapter 15), Engineering Materials (Chapter 12) and Instrumental Methods of Analysis (Chapter 10) have been dealt with appropriately.

Hence, this book proves to be a very good reference for updating knowledge and creating awareness of recent techniques and processes.

Dedicated Web Support

Readers are encouraged to login at our website http://www.mhhe.com/sivasankar/ec which contains a wealth of digital content. Instructors can access Solutions Manual and PowerPoint slides, which can be used as teaching aids. Students can refer web links for in-depth research, and additional problems for practice. The website also features model question papers with solutions—an effective guide for exam preparations.

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1

THERMODYNAMICS

1.1 Introduction

Thermodynamics means heat power and this branch of physical science deals with the interconversion of energy that accompanies all changes that occur in nature. For example, motion of a particle, combustion of coal, growth of tissue in a living species etc., are diverse processes that are accompanied by interconversion of energy. The most common form of energy is heat which may be formed from chemical energy, mechanical or electrical energy and in turn is converted into any of these forms. Thermodynamics may be studied by any of the two approaches, namely, classical and statistical. *Classical thermodynamics* also called *reversible* or *equilibrium thermodynamics* deals with macroscopic or bulk properties of matter observable our day-to-day life. *Statistical thermodynamics* involves the application of classical or quantum mechanics in the evaluation of thermodynamic properties of a large collection of atoms and molecules in a microscopic view point. Properties of substances subjected to extremes of temperature and pressure can be predicted by a statistical approach combining the computational techniques with quantum mechanics. Classical thermodynamics provides solutions to most engineering problems by considering changes in macroscopic properties and hence this chapter deals with this approach. Thermodynamics is based mainly on two laws, the first and second laws of thermodynamics. These laws are based on experimental observations on macroscopic systems and are applicable to all phenomena in nature. These laws have been accepted as no contradictory evidence has yet been obtained.

The first law of classical thermodynamics deals with direct conversion of heat into other forms of energy. Energy changes that accompany processes are considered, but the law is not concerned with the direction in which such changes in energy occur. The first law is useful in the quantitative study of energy changes in chemical reactions (thermochemistry) and in heat-mechanical work relationship. The second law of thermodynamics specifies the direction of energy changes and is useful in predicting quantitatively the energy released and the formation of products in chemical reactions under a given set of conditions.

Thermodynamics deals with systems in equilibrium and is not concerned with the rate at which equilibrium is attained as time is not considered as a variable and hence does not appear in thermodynamic equations. The rate of chemical processes is the domain of kinetics.

1.2 Terminology

Thermodynamics is an abstract science with terms and language which need to be defined and understood.

1.2.1 System, surroundings and boundaries

A *system* in thermodynamics is defined as a part of the matter separated from its *surroundings* by arbitrarily chosen, imaginary or real *boundaries*. The system chosen may be investigated either theoretically or experimentally. A theoretical system is ideal and amenable for mathematical analysis while an experimental system is a real one. The system is homogenous if it contains a single phase having physical and chemical properties identical throughout the system. A heterogeneous system will have more than one phase each phase having its own distinct physical and chemical properties. *Surroundings* include other systems in the immediate vicinity of the chosen system. The surroundings interact with the chosen system by an exchange of matter or energy. One may consider a gas (system) in a balloon (boundary) surrounded by air (surrounding) or a liquid (system) in a beaker (wall of the beaker being the boundary) immersed in a water bath (surrounding) as examples of the terms defined. Any change in the surroundings brings a change in the system but not in the boundary. A boundary may permit flow of heat into or out of the system if it is *diathermic*. In contrast an *adiabatic* boundary (e.g., walls of a thermos flask) does not permit heat transfer. Depending on the nature of the boundary three types of systems are identified. (i) *Isolated system*; one which cannot exchange matter or energy with its surroundings and whose mass and energy remain constant. No work can be done by or on this system. An example of an isolated system is a reaction occurring in a sealed vessel completely insulated from its surroundings. The universe can be considered as an isolated system as it does not have any surroundings. However, a perfectly isolated system does not exist. (ii) *Closed system* allows exchange of energy but not matter with its surroundings e.g., a sealed flask containing a gas or a liquid surrounded by a water bath, the walls of the flask permit only heat transfer to the water in the bath whose temperature can thus be altered. Such a closed system permits exchange of heat or work between the system and its surroundings but not the contents (matter). (iii) *Open system* is capable of exchanging both matter and energy with its surroundings. Examples of open systems include living systems which interact with surroundings exchanging matter and energy or reactions conducted in open vessels.

1.2.2 State of system and process

The *state* of a system is defined by characteristic macroscopic properties such as temperature (T), pressure (P), volume (V), mass (M), composition (C), etc. A system is said to have undergone a change of state when one or more of these properties (variables) change from their initial values. A system undergoes a change from one state to another by a path which is specified by giving the initial state of the system, the sequence of intermediate steps and the final state. The path by which a system undergoes change from an equilibrium state to another over a period of time is called a *process,* which describes the manner of change. Thus an *isothermal process* occurs at constant temperature. A system under goes an isothermal process when it is surrounded by a thermostat and maintains a constant temperature by exchanging heat with the surroundings. A system such as a reaction occurring in an open vessel at atmospheric pressure is said to undergo *isobaric process* (change of state at constant pressure). Isobaric process is always accompanied by a volume change. *Isochoric process* involves change of state under constant volume. In an *adiabatic process* heat is not allowed to enter or leave the system. The system is thermally insulated and the temperature of the system may increase or decrease. A process is considered as a *cyclic process* if a system undergoes change from state 1 to 2 by a certain path and returns to its original state by the same or a different path then the system is said to have gone through a cycle of change.

1.2.3 State functions

Thermodynamic properties which depend only on the present state of the system and are independent of the past history or the path by which the state was reached are called state functions. These include the macroscopic properties already mentioned in the previous paragraph as well as other properties such as internal energy (E), enthalpy (H), entropy (S), free energy (G), etc. Each state function has a definite value for a given state. Since a state function depends only on the present state of a system, a change in any state function depends only on the initial and final states of the system and not on the path of change. The change in a state function in a cyclic process is equal to zero.

Two types of state functions or properties are characteristic of a system. Properties which depend on the amount of the substance present in the system are called *extensive properties*. The mass and volume of a system are examples of extensive properties. Properties which are independent of the amount of substance present in the system are called *intensive properties* or *intensive factors*. Examples of intensive properties include temperature, viscosity, refractive index, surface tension etc. which have the same value in any part of the system at equilibrium. Extensive properties are additive whereas intensive properties are not. The value of an intensive property is the same in any part of the system at equilibrium. An extensive property becomes an intensive property once the unit amount is specified. Thus mass and volume are extensive properties, but density (mass/unit volume) and specific volume (volume/unit mass) are intensive properties. Similarly heat capacity is an extensive property whereas specific heat is intensive. In general the ratio of two extensive properties is intensive. Changes in the energy are the multiplication products of an extensive property with an intensive property. Thus the heat energy absorbed by a system is given as the product of the mass and specific heat.

1.2.4 Equilibrium

A system is said to be in a state of equilibrium if its properties remain constant and do not change with time. A system is in thermal and mechanical equilibrium if its intensive properties such as pressure and temperature remain the same in any part of the system. If the chemical composition of the system remains unaltered with time the system is said to be in chemical equilibrium. A system in thermal, mechanical and chemical equilibrium is said to be in *thermodynamic equilibrium* and thermodynamics is primarily concerned with a study of systems in equilibrium. A system exists in a non-equilibrium state, for example, the temperature or pressure may be different in different regions of the same system. If the relaxation time, that is, the time required to restore equilibrium conditions is longer compared to an observable time then the system is said to be in a *metastable state*, a state which appears to be in a state of equilibrium even though it is actually in a non-equilibrium state. For example, the high temperature forms of silica, namely, crystobalite and trydimite (metastable states) exist simultaneously in the earth's crust as they do not change over to the thermodynamically stable quartz within a reasonable time limit.

1.2.5 Reversible and irreversible processes

A process is said to be *reversible* when a system undergoes a change from one state to another through a number of steps, the system being in equilibrium with its surroundings with respect to temperature and pressure at each step. The energy change with each step, in a reversible process can be reversed in its direction by small or infinitesimal changes in the thermodynamic variables such as temperature or the pressure acting upon the system. A system which has undergone a reversible process can be restored to its original or initial state with an infinitesimal change in the external system. Two important requirements for a process to be reversible are (i) the process must be carried out slowly through a number of states of infinitesimal change and (ii) the process must not experience any friction, and there should not be finite temperature differences. Reversible processes are thus theoretical or imaginary. However, it is possible to approach closely the condition of reversibility at least in a few cases. An example of such a process occurs in a Daniel cell in which the chemical energy is converted into electrical energy in the galvanic cell and by applying an emf from an external source slightly greater than that generated by the galvanic cell, the direction of energy flow is reversed and the electrical energy can be converted into chemical energy.

An *irreversible process* is one in which the system or its surroundings undergo fast and sudden changes and are not restored to their initial state. Almost all natural processes are irreversible processes. Examples include the flow of water downhill, flow of heat from a hot body or a region of higher temperature to a cold body or region of lower temperature, flow of gases from a high pressure region to a low pressure region etc. Irreversible processes are also called *spontaneous processes* since the direction of the process is spontaneous.

Reversible processes are amenable for mathematical analysis. The state functions associated with the initial and final states of a system undergoing changes irreversibly may be computed by considering a hypothetical reversible path.

1.2.6 Measurement of temperature

The science of measurement of temperature called *thermometry* is based on the ***zeroth law of thermodynamics***, according to which *two systems in thermal equilibrium with a third system are in thermal equilibrium with each other*. Measurement of temperature depends on the changes in observable physical properties such as a volume change of a liquid (e.g., mercury or ethanol) held in a capillary tube, emf in a thermocouple, or a variation of electrical resistance of metal or its oxide (in a thermistor), etc. The temperature indicated by the temperature measuring device or thermometer is taken as the temperature of the system because the thermometer and the system are in thermal equilibrium with each other. Measurement of temperature depends on the measurement of the physical property at two fixed points and assuming a linear property-temperature relationship between the two fixed points. Thus freezing point of water (ice point) and boiling point of water (steam point) at one atmospheric pressure were fixed as the lower reference point (0 in Celsius and 32 in Fahrenheit scales) and the higher reference point (100 in Celsius and 212 in Fahrenheit scales) respectively. The volume changes of liquids between the two fixed points are assumed to be linear with temperature. In order to have a temperature scale independent of the nature of the thermometric substance; an *absolute scale* or *Kelvin scale* of temperature was proposed using an ideal gas as the thermometric substance. The absolute scale is based on the variation of the pressure of a given mass of ideal gas at constant volume, with temperature as given by the equation.

$$P_t = P_0(1 + \alpha_p t) \tag{1.1}$$

where P_t and P_0 are the pressures of the gas at $t°$ C and 0° C respectively and α_p is the coefficient of pressure change. The value of the coefficient (fraction by which the pressure increases for every degree rise in temperature) was determined to be 36.61×10^{-4}° C^{-1} equal to 1/273.15 for all gases in Celsius scale and 459.7 in Fahrenheit scale. The absolute temperature T can be written as

$$T = 1/\alpha_p + t \tag{1.2}$$

$T = 273.15 + t$ in Celsius scale or $459.7 + t_F$ in Fahrenheit scale.

The value of $T = 273.15$ K if $t = 0°$ C and $T = 0$ K if $t = -273.15°$ C. The absolute zero of temperature is the lowest conceivable temperature.

1.2.7 Heat, work and energy

When two systems having different temperatures are in contact with each other, heat flows from the system having a higher temperature to the one at a lower temperature. Heat is the energy transferred because of the temperature difference between the systems. The amount of heat transferred q (or energy change) is proportional to the difference in temperature ΔT or $q = CT$ where C is the *heat capacity* defined as the quantity of heat required to raise the temperature of a body by one degree. Heat capacity is an extensive property as it depends on the amount of the substance as well as the nature of the substance. The quantity of heat required to raise the temperature of one gram of the substance by 1° C is called *specific heat* and the amount of heat required to raise the temperature of one mol of a substance by 1° C is called *molar heat capacity*. The quantity of heat is expressed in calories, one calorie is defined as the quantity of heat required to raise the temperature of 1 g of pure water by 1° C at 15° C (1 cal = 4.184 J).

The energy of a system is its capacity to do work and the transfer of energy between systems or system and surroundings may occur through work. Work can be done by a system only when it is mechanically linked to its surroundings and when it is moving against some force originating from the surroundings acting on the boundary. The work may be in the form of expansion or compression called the pressure-volume work. The pressure-volume work may be explained by considering a system such as a cylinder having a cross-sectional area A containing an ideal gas and fitted with a weightless and frictionless piston. It is necessary to consider the hypothetical situation of a weightless piston to know accurately the external pressure and a frictionless piston because friction will cause heat and we are considering only the energy transfer in the form of work and not heat. If the gas is allowed to expand against the opposing external pressure P resulting in the displacement of the piston by a distance dr the infinitesimal work done by the gas is

$$\delta w = F.\mathrm{d}r \tag{1.3}$$

where the force F acting on the piston is given as the product of external pressure P and the cross-sectional area of the cylinder A and hence the above equation may be written as

$$\delta w = P.A.\mathrm{d}r \tag{1.4}$$

Since the product A.$dr = \mathrm{d}V$, the volume swept by the piston while moving by a distance dr,

$$\delta w = P.\mathrm{d}V \tag{1.5}$$

Thus the work done by the gas is equal to a change in volume against the pressure P. The symbol δ is used to indicate that the quantity considered is not an exact differential while the symbol d is used to indicate that changes in properties are exact differentials. The total amount of work done by the gas is obtained by integration of the volume change that occurred between initial value V_i and the final value V_f.

$$\text{Total work done} = \int_{\text{initial}}^{\text{final}} P.dv \tag{1.6}$$

Work done by a system may be in the form of mechanical, electrical or gravitational work. Thus energy is the property of the system and the transfer of energy appears as heat or work and hence these are not properties of the system. Energy has the dimensions of mass × $(\text{length})^2$ × $(\text{time})^{-2}$ and is expressed in units of ergs, joules or calories while work is expressed in ergs (dyn-cm) or in joules (Newton-meters, N-m or volt-coulombs).

1.3 First Law of Thermodynamics

The first law of thermodynamics also known as the *principle of conservation of energy* was enunciated by Clausius, Kelvin and Helmholtz based on a number of experimental observations. The law may be stated in more than one way as follows:

Energy can neither be created nor destroyed but it can be transformed from one form into another. Or *The total energy of the system and its surroundings must remain constant.*

Einstein's relationship $E = mc^2$ indicates that energy can be created by the destruction of mass, as if contradicting the first law of thermodynamics. But it should be noted that in any energy conversion, conservation of mass and energy together is to be considered. In chemical reactions the conversion of mass into energy is negligible and hence the first law is concerned only with the conservation of energy alone.

Every system has a store of energy called the ***internal energy*** or ***total energy*** E which depends on the pressure, volume, temperature, mass and composition of the system. It includes all forms of energy associated with the system such as potential energy, kinetic energy, vibrational energy, rotational energy etc. of the constituent atoms and molecules and the manner in which the atoms are bonded in the molecules. It is a state function and hence the absolute value of the internal energy of a system cannot be measured, but changes in the internal energy can be measured in terms of the heat and work exchanged between the system and its surroundings.

The direction of the transfer of energy in the form of heat (q) or work (w) between a system and its surroundings is indicated by a sign convention as follows. Heat gained or absorbed by a system is given a positive sign (+q) and heat evolved from the system or lost by the system is given a negative sign (–q). Similarly the work done by the system on the surroundings (e.g., expansion of a gas) is given a positive sign (+w) while work done on the system (e.g., compression of a gas) a negative sign (–w).

The first law of thermodynamics can thus be expressed in a mathematical formulation as

$$q = \Delta E + w \text{ or } \Delta E = q - w \tag{1.7}$$

For infinitesimal changes, the above equation may be written as

$$dE = \delta q - \delta w \tag{1.8}$$

The total energy of a system and its surroundings must remain constant in a cyclic process in which the system goes from one state to another and returns to its original state through a series of steps; $\Delta E = 0$ and hence $q = w$, that is work done is equal to the heat absorbed.

In an isolated system neither heat nor work is exchanged and hence the total energy of the system remains unchanged. There is no transfer of mass also in an isolated system and hence both mass and energy remain unaltered. An isolated system does not do any work or work cannot be done on the system. In an open system; matter, heat and work can be exchanged between the system and its surroundings.

1.3.1 Enthalpy–heat change in chemical systems

Chemical reactions are always accompanied by heat changes and the reactions are classified into two categories on the basis of whether heat is evolved or absorbed. Reactions in which heat is absorbed are called *endothermic* and those in which heat is evolved are called *exothermic*. Reactions are carried out either in closed vessels at constant volume or open to atmosphere at constant pressure. For reactions occurring at constant volume and considering the work to be only of pressure-volume work, the first law of thermodynamics may be written as

$$dE = \delta q - PdV \tag{1.9}$$

Since $dV = 0$ no mechanical work is done and $\delta w = 0$. Hence for reactions taking place at constant volume the heat exchanged between the system and its surroundings is a direct measure of the change in the internal energy of the system.

$$dE = \delta q \tag{1.10}$$

For reactions carried out at atmospheric pressure (constant pressure), and under the constraints that the pressure within the system is equal to the pressure of its surroundings and remains constant, and considering only expansion as work it may be written for a finite change as

$$\Delta E = E_2 - E_1 = q - w = q - P(V_2 - V_1) \tag{1.11}$$

where E_2 and E_1 are the internal energies of the final and initial states and V_2 and V_1 are the volumes of the final and initial states.

Rearranging Eq. 1.11 gives

$$q_p = (E_2 + PV_2) - (E_1 + PV_1) \tag{1.12}$$

where q_p is the heat transferred at constant pressure. Just as E, P and V are state functions (E + PV) is also a state function and may be given as

$$H = E + PV \tag{1.13}$$

H is called ***enthalpy*** (Gk. to warm in). So Eq. 1.12 may be written as

$$q_p = H_2 - H_1 = \Delta H \tag{1.14}$$

Thus a change in enthalpy is equal to the amount of heat absorbed or evolved for chemical reactions occurring at constant pressure.

The relationship between the two state functions, total energy and enthalpy of a system may be deduced. For a system in which both the pressure and volume vary, the enthalpies of the final and the initial states and the total energies may be expressed as

$$H_2 - H_1 = E_2 - E_1 + P_2V_2 - P_1V_1 \tag{1.15}$$

$$\Delta H = \Delta E + \Delta(PV) \tag{1.16}$$

If pressure is constant then Eq. 1.16 becomes

$$\Delta H = \Delta E + P.\Delta V \tag{1.17}$$

$$q_p = q_v + P.\Delta V \tag{1.18}$$

The heat absorbed at constant pressure is used for increasing the internal energy of the system as well as to do work of expansion while the heat absorbed at constant volume is used only for increasing the internal energy of the system and no work is done. Thus $\Delta H > \Delta E$. However, in a compression process ΔV is negative and hence $\Delta H < \Delta E$. For processes involving solids and liquids ΔV is negligibly small and hence $\Delta H \sim \Delta E$. In the case of reactions involving gases ΔV is appreciable and cannot be neglected. For example in a hypothetical reaction involving ideal gases at constant pressure represented by a stoichiometric equation as

$$aA = bB \longrightarrow cC + dD \tag{1.19}$$

Using the ideal gas equation

$$PV = nRT \tag{1.20}$$

$$P(\Delta V) = P(V)_{\text{products}} - P(V)_{\text{reactants}} = P(nRT)_{\text{products}} - P(nRT)_{\text{reactants}}$$

$$P(\Delta V) = RT.\Delta n \tag{1.21}$$

where Δn is the change in the number of mols of gases, that is, the difference between the number of molecules of products and reactants as given in the stoichiometric equation. The enthalpy change for the above reaction may now be written as

$$\Delta H = \Delta E + RT\Delta n \tag{1.22}$$

1.3.2 Application of first law of thermodynamics

A few of the applications of the first law of thermodynamics relevant to chemical systems are given in this section.

(i) Molar heat capacity (C) is the amount of heat required to raise the temperature of one mol of a substance by 1° C and may be expressed as the rate of change of heat with temperature

$$C = \delta q/\mathrm{d}T \text{ for 1 mol of substance} \tag{1.23}$$

From the first law of thermodynamics (Eq. 1.9) since $\delta q = \mathrm{d}E + P\mathrm{d}V$

$$C = \frac{\mathrm{d}E + P\mathrm{d}V}{\mathrm{d}T} \tag{1.24}$$

Molar heat capacity varies with pressure as well as temperature and hence can be expressed at constant volume (C_v) and at constant pressure (C_p). At constant volume $\mathrm{d}V = 0$ and hence Eq. 1.24 may be written as

$$C_v = \frac{\mathrm{d}E}{\mathrm{d}T} \tag{1.25}$$

or in terms of partial differentials $C_v = \left[\frac{\partial E}{\partial T}\right]_V$ (1.26)

Thus molar heat capacity at constant volume is defined as the increase in the internal energy of the system per degree rise in temperature.

At constant pressure Eq. 1.24 may be written as

$$C_p = \frac{\mathrm{d}E}{\mathrm{d}T} + P\left[\frac{\mathrm{d}V}{dT}\right] \tag{1.27}$$

or in terms of partial differentials as $C_p = \left[\frac{\partial E}{\partial T}\right]_P + P\left[\frac{\partial V}{\partial T}\right]_P$ (1.28)

Differentiating Eq. 1.13 with respect to temperature at constant pressure gives

$$\left[\frac{\partial H}{\partial T}\right]_P = \left[\frac{\partial E}{\partial T}\right]_P + P\left[\frac{\partial V}{\partial T}\right]_P \tag{1.29}$$

Combining Eqs. 1.28 and 1.29 molar heat capacity at constant pressure is given as

$$C_P\left[\frac{\partial H}{\partial T}\right]_P \tag{1.30}$$

For the liquids and solids $\Delta H \sim \Delta E$ and hence C_p and C_v are similar but are different for gases. For an ideal gas $C_p - C_v = R$

(ii) Ideal gases have a simple equation of state as $PV = n\,RT$ and application of the first law to ideal gases implies the calculation of changes in state functions of internal energy (ΔE) and enthalpy (ΔH) and path functions of heat exchanged (q) and work done (w). The values of path functions depends on the path followed in the change of state. There are four different paths or process conditions through which a change of state can be effected in an ideal gas. These include (i) constant pressure or isobaric process ($\mathrm{d}P = 0$), (ii) constant volume or isochoric process ($\mathrm{d}V = 0$), (iii) constant temperature or isothermal process ($\mathrm{d}T = 0$) and (iv) adiabatic process ($\delta q = 0$).

(i) Isobaric process: At constant pressure and a finite change in volume from V_1 to V_2, the total work can be given as

$$w = P(V_2 - V_1) = P\,\Delta V \tag{1.31}$$

The work w will be positive (work done by the gas) when $V_2 > V_1$ (expansion) and w is negative (work done on the gas) under compression. For one mol of an ideal gas $PV = RT$ and hence

$$w = R\,(T_2 - T_1) \tag{1.32}$$

The relationship between heat transferred at constant pressure q_p, change in enthalpy ΔH and the molar heat capacity at constant pressure C_p may be expressed as

$$\Delta H = q_p = C_p\,(T_2 - T_1)$$

(taking C_p to be constant in the temperature range) (1.33)

Similarly $$\Delta E = q_p - w = C_v\,(T_2 - T_1) \tag{1.34}$$

(ii) Isochoric process: At constant volume V_2 and $\mathrm{d}V = 0$ the following relationships hold good

$$w = \int_1^2 P\mathrm{dV} = 0 \tag{1.35}$$

$$q_v = \mathrm{C_v}\,(T_2 - T_1) \qquad (\mathrm{C_v} \text{ remains a constant}) \tag{1.36}$$

$$\Delta E = q_v - w = q_v = C_v(T_2 - T_1) \tag{1.37}$$

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + R(\Delta T) \tag{1.38}$$

$$= C_v\,(T_1 - T_2) + R\,(T_1 - T_2) \tag{1.39}$$

($T_1 > T_2$ since $P_1 > P_2$ and q_v is negative)

$$= C_p(T_1 - T_2) \tag{1.40}$$

(iii) Isothermal process: Temperature remains constant at T_1 and $\mathrm{d}T = 0$. The isothermal process may be considered as equivalent to expanding the gas isobarically and compressing it isochorically. The relevant equations for calculating the parameters are

$$w = RT\ln\,(V_2/V_1) \qquad (\text{since } \Delta E = 0 \text{ and } q = \mathrm{w}) \tag{1.41 a}$$

$$= RT\ln\,(P_1/P_2) \tag{1.41 b}$$

$$\Delta H = \Delta E + R\,\Delta T = 0 \tag{1.42}$$

(iv) Adiabatic process: The system is thermally insulated and there is no exchange of heat between the system and its surroundings. Hence $q = 0$.

$$w = \Delta E \tag{1.43}$$

If expansion occurs work is done by the system (–w) and heat is taken from the system, hence, the internal energy and temperature decrease. On the other hand, during compression, work is done on the system and hence internal energy and temperature increase.

$$\Delta E = C_v\mathrm{d}T = C_v\,(T_2 - T_1) \tag{1.44}$$

$$\Delta H = C_p\,(T_2 - T_1) \tag{1.45}$$

(iii) Thermochemistry involves the measurement and analysis of heat changes that accompany physical or chemical transformations in a calorimeter. The reaction vessel is surrounded by water in the calorimeter and it is assumed that any heat evolved during a reaction is used only to raise the temperature of water in the calorimeter and the increase in temperature ΔT is accurately measured. The heat absorbed in an endothermic change or liberated during an exothermic change is called the heat of reaction. Heat

of reaction at constant volume is equal to ΔE. Since most of the reactions occur at constant pressure the heat of reaction is usually expressed in terms of enthalpy change (ΔH) accompanying the reaction. The enthalpy of reaction (ΔH) is the difference between the enthalpies or heat contents of the products and reactants

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \tag{1.46}$$

Heat changes accompanying the transformations, whether ΔE or ΔH, are expressed for one mol of the reactant. Depending on the nature of the physical or chemical transformation taking place the enthalpy change is designated appropriately. Thus heat of combustion (ΔH_c) is the change in enthalpy when one mol of the substance is completely burnt in excess of oxygen. Heat of formation (ΔH_f) of a compound is the change in enthalpy when one mol of the compound is formed from its elements in their commonly occurring (or standard) states. It is assumed arbitrarily that the enthalpy of an element in its standard state is zero, the standard state being defined as the most stable physical form at one atmospheric pressure and temperature of 298 K. The enthalpy of formation of a compound is indicative of the stability of the compound. In general, the lower the enthalpy of formation of a compound the more is its stability because the stability of a compound is inversely proportional to its heat content (intrinsic energy). Thus the enthalpy of a stable compound is negative, that is, its energy content is less than the sum of its constituent elements. On the other hand if enthalpy of formation of a compound is positive the compound is unstable. Other commonly encountered heat changes include the enthalpy of fusion (heat change accompanying when one mol of a substance is transformed from the solid to liquid state at its melting point), enthalpy of vaporisation (heat change accompanying when one mol of a substance is transformed from the liquid to vapour state at its boiling temperature), enthalpy of sublimation (heat change accompanying when one mol of a substance is transformed directly from the solid to vapour state at a given temperature), enthalpy of neutralisation (heat change accompanying when one gram-equivalent of an acid in dilute aqueous solution is neutralised by one gram-equivalent of a base and vice - versa) and enthalpy of formation of chemical bond or bond energy.

A direct consequence of the first law is the thermochemical law called *Hess's law of constant heat summation.* It is based on the concept of state function according to which any finite change in a state function such as the E or H depends only the initial and final states of the system and not on the paths through which such changes are brought about. The law states: *the total heat change in any chemical reaction is the same whether the reaction takes place in a single step or in several stages.* For example, the formation of CO_2 may be considered to occur in a single step

$$\text{C(graphite)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)};\ \Delta\text{H} = -\,393.5\ \text{kJ} \tag{1.47}$$

Or in two steps involving the formation of CO in the first step which is converted to CO_2 in the second step as

$$\text{C(graphite)} + \tfrac{1}{2}\,\text{O}_2\text{(g)} \longrightarrow \text{CO(g)};\ \Delta\text{H} = -\,110.5\ \text{kJ} \tag{1.48}$$

$$\text{CO(g)} + \tfrac{1}{2}\,\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)};\ \Delta\text{H} = -\,283.0\ \text{kJ} \tag{1.49}$$

Thus, the heat of formation of CO_2 from the elements is the same (–393.5 kJ) whether the formation occurs in a single step or in two steps. Thus Hess' law is useful for calculating the heat changes in chemical reactions.

The effect of temperature on heat of a reaction is given by Kirchoff's equation as

$$\Delta H = H_P - H_R \tag{1.50}$$

where $H_P = \sum H$ (products) and $H_R = \sum H$ (reactants). On differentiating the Eq. 1.50 with respect to temperature Kirchoff's equation is obtained.

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial H_P}{\partial T}\right)_P - \left(\frac{\partial H_R}{\partial T}\right)_P \qquad (1.51)$$

A similar equation can be written for the variation of ΔE with temperature.

(iv) Bond energy or the *heat of formation of a bond* may be defined as the average amount of energy (enthalpy change) required to break one mol bonds in a gaseous molecule to form gaseous fragments, atoms, radicals etc. It is more appropriate to call bond energy as bond enthalpy as it is calculated from measurements at constant pressure and is different from *bond dissociation energy* which is defined as the energy required to break a given bond in a compound. The bond energy depends on the molecular environment. For example the energy required to break the H–OH bond in water is 119.95 k.cal/mol (501.9 kJ/mol) while the energy required to break the O–H bond in hydroxyl radical is only 101.19 k.cal/mol (423.4 kJ/mol). The sum of these values is the dissociation energy of water (221.14 kcal/mol = 925.25 kJ mol^{-1}) that is the energy required to break the two O–H bonds in water and hence the average bond energy for the O–H bond in water is (221.14/2) = 110.57 k.cal/mol (462.6 kJ/mol). In the case of polyatomic molecules of the type AB_n the average bond energy of A–B may be calculated by dividing the heat of formation of the compound with the number of bonds n. Thus for CH_4 the average bond energy of C–H bond is the heat of formation divided by 4 = 397.4 /4 = 99.4 k.cal/mol (415.9 kJ/mol).

The bond energy of a bond is almost the same, irrespective of the compound in which it is found. Chemical reactions involving the breaking of bonds in reactant molecules which are endothermic and making of bonds in the product molecules which are exothermic. The greater the energy required to break a bond the stronger is the bond. The net change in bond energy during a chemical reaction involving bond breaking and bond making represents the enthalpy change of the reaction. Thus, it is possible to calculate approximately the enthalpy change of a chemical reaction by considering the bond energies of the bonds that have been broken and of those which are formed.

(v) Explosions may be regarded as taking place under adiabatic conditions as they are too fast to allow for the transfer of heat into the surroundings. The heat evolved during the reaction is utilised in heating the products of the reaction. The maximum flame temperature and the maximum explosion temperature may be calculated on the basis of adiabatic conditions. Changes in the internal energy. ΔE and enthalpy ΔH are utilised for heating the reaction products to the final temperature. The reaction is assumed to take place in two steps between the same temperatures of initial temperature T_1 (298 K) and the final temperature T_2. For the process at constant pressure, the final temperature is the flame temperature and at constant volume the final temperature is taken as the explosion temperature. The final temperature T_2 to which the products are heated is calculated using Kirchhoff's equation. Assuming that C_p remains constant in the temperature range T_1 to T_2 the flame temperature may be calculated from the equation.

$$T_2 - T_1 = \frac{-(\Delta H)}{C_P} \qquad (1.52)$$

The explosion temperature may similarly be calculated using ΔE and C_v because explosion is considered as a constant volume process.

(vi) Joule-Thomson effect is of practical importance in the liquefaction of gases. An ideal gas has no intermolecular attraction and hence the product PV remains a constant at any given temperature at all pressures. When such a gas expands under adiabatic conditions into a vacuum, no heat is absorbed or evolved, no external work or work to separate the molecules has to be performed. Hence $q = 0$, $w = 0$ and $\Delta E = 0$. However when a real gas under high pressure is allowed to expand into vacuum or

a low pressure region, the temperature of the gas decreases as noticed by Joule and Thomson (Lord Kelvin). This was attributed to the fact that work was done by the gas in overcoming the intermolecular attractive forces between the gas molecules at the expense of the kinetic energy (internal energy) resulting in the decrease of the temperature of the gas.

1.3.3 Limitations of the first law

The first law specifies that energy of an isolated system remains constant and that one form of energy can be converted into another. It also states, that energy is neither created nor destroyed. However, the first law does not indicate whether such a conversion is feasible and if so to what extent. It is well known that water flows downhill and that heat flows from a hot body to a colder one till the two reach a common temperature. Such processes occur naturally without the aid of any external agency and are called *spontaneous processes*. The spontaneous process by which a system proceeds from a non-equilibrium state to an equilibrium state is also called *an irreversible process*. A system always exhibits a natural tendency to proceed towards equilibrium and on attaining equilibrium it does not return to its initial condition on its own unless disturbed by external agencies. Though from experience it is possible to predict the feasibility of the natural processes mentioned above, the first law does not provide any criterion to predict the feasibility. The lack of criterion to predict the feasibility of a physical or chemical process is a limitation of the first law. Thus, on the basis of the first law we cannot predict whether a reaction will occur when two chemicals are mixed.

The first law also establishes the relationship between the state functions of internal energy and enthalpy. Accordingly ΔE is the heat change occurring in a process at constant volume and ΔH is the heat change occurring at constant pressure. However it does not specify the direction of heat change or flow. Most of the spontaneous chemical reactions at constant pressure are exothermic, leading to a conclusion that a reaction would proceed in that direction in which $\Delta H < 0$. However, many endothermic reactions in which $\Delta H > 0$, also occur spontaneously (e.g., synthesis of ammonia or nitric oxide). Thus the first law is unable to predict the direction of heat flow.

The first law establishes the relationship between heat and work and the conversion of heat to work. On the basis, that energy can neither be created nor destroyed but only transformed, one would expect that heat could be converted completely into mechanical work. The conversion of heat into useful mechanical work is industrially important. However, experience has shown it to be otherwise.

Joule and Thomson concluded on the basis of their experiments regarding heat energy and mechanical work that by spending 4.18 joules of mechanical energy or work one can realise 1 calorie of heat. This is known as *mechanical equivalent of heat*. However, in the reverse direction 1 calorie of heat does not produce 4.18 joules of mechanical work and a part of the heat energy is lost to the surroundings. Thus 100 percent conversion of heat energy into mechanical work is not achieved. However the total energy is conserved when the mechanical work and the heat dissipated are taken into account.

Carnot's theoretical treatment of a reversible heat engine showed that the conversion of thermal energy completely into work is not possible. A heat engine takes heat from a source, converts some of it into useful work and discards the rest to a sink and this operation is possible only if the source is at a higher temperature compared to the sink. The efficiency of a heat engine ε, is given as

$$\varepsilon = \frac{\text{Net work done by the system(engine)}}{\text{heat absorbed by the engine}} = w/q \qquad (1.53)$$

where w is the net work done by the engine and is equal to the difference between the heat absorbed by the engine from the source (q_h) and the heat discarded to the sink (q_c).

Carnot's theoretical treatment also resulted in a statement that all reversible engines operating between the same two temperatures have the same efficiency. This efficiency is independent of the nature of the working substance and depends only on the quantities q_h and q_c.

These limitations necessitated the introduction of another physical law, namely the second law of thermodynamics, based on experience.

1.4 The Second Law of Thermodynamics

The second law of thermodynamics is based on the principle of asserting the impossibility of carrying out a process. The law has been stated in many ways. According to Kelvin and Planck *in any process it is impossible to convert the heat absorbed from a reservoir completely into work.* It means that only a fraction of heat can be converted into work and the rest of the thermal energy is unavailable for conversion. It also means that heat exchange with a single reservoir cannot be harnessed to do mechanical work. According to Clausius *heat cannot by itself flow from a cold to a hot body (spontaneously) without the intervention of an external agency.*

1.4.1 Entropy

Absorption of heat by a system increases its energy. Since heat energy is not an organised form of energy (unlike electrical, chemical or mechanical energy) it enhances the disorderly or random motion of atoms and molecules in a substance (system). In contrast mechanical work involves an orderly transformation of the system from one state to another. It is possible to convert the organised form of energy completely into heat energy. However, it is not possible to convert heat energy completely into mechanical work or any of the organised forms of energy. A portion of the heat energy is dissipated to the surroundings. The conversion of an organised form of energy into heat energy is always accompanied by an increase in the disorder of the system.

A new thermodynamic function called *entropy*, which is a measure of disorder, becomes necessary to explain spontaneous processes. The term entropy (Gk. = change) was coined by Clausius and the second law of thermodynamics uses entropy to identify spontaneous changes without violating the principle of conservation as stated by the first law. Entropy is represented by the symbol S. Since entropy is a state function its values depend only on the initial and final states of the system and independent on the path of change. Entropy is expressed in units of joules per Kelvin (jK^{-1}) and since entropy is an extensive property it is expressed for one mol of the substance as molar entropy in $jK^{-1}mol^{-1}$. The change in entropy of the system ΔS is given as

$$\Delta S = q_{rev}/T \tag{1.54}$$

The second law of thermodynamics may also be stated in terms of entropy as *the change in entropy of an isolated system is always positive when it undergoes a spontaneous process.* All natural processes are spontaneous and irreversible and hence are accompanied by a net increase in entropy. Thus the entropy of the universe (an isolated system) increases with every change that occurs in nature. When the entropy of the universe reaches a maximum and an equilibrium is attained it will result in an entropic doom. Using these ideas Clausius put forth the first law of thermodynamics as *'the energy of the universe is constant'* and that of second law as *'the entropy of the universe tends always to a maximum'*.

1.4.2 Entropy changes in spontaneous processes

Thermodynamically irreversible processes are spontaneous and hence must be accompanied by an increase in entropy. The change in entropy of an isolated system ΔS_{total} consisting of the system of interest (ΔS) and its surroundings (ΔS_{sur}) is the sum of the $\Delta S + \Delta S_{sur}$ and is always positive for spontaneous processes.

$$\Delta S_{total} = \Delta S + \Delta S_{sur} \geq 0 \tag{1.55}$$

1.4.3 Entropy changes for a reversible process

In reversible processes the system undergoing a change between two states, is in equilibrium with its surroundings at every infinitesimal change. The energy exchanged between the system and its surroundings in the form of $+\delta q$ (heat absorbed by the system) is equal to $-\delta q_{rev}$ (heat dissipated to the surrounding) at a given temperature T and hence

$$dS = \delta q_{rev}/T \tag{1.56}$$

For a measurable or finite change in the system the change in entropy ΔS of the system is the integral of infinitesimal changes

$$(S_2 - S_1) = \int_1^2 \delta\, qrv/T \tag{1.57}$$

where S_2 and S_1 represent the entropies of the final and initial states of the system respectively. The entropy change of a system between two states can be determined by determining the heat necessary to take it along a reversible path, between the same two states. For a reversible process the heat exchanged as well as the work exchanged should be reversible and for a reversible cyclic process

$$\Sigma\, q_{rev}/T = 0 \text{ or } \Delta S = 0 \tag{1.58}$$

The change $\Delta S_{total} = 0$ for a reversible process and ΔS for the system $= 0$ at equilibrium.

For reversible adiabatic processes, δq is zero and hence ΔS is always zero. Reversible adiabatic processes are isoentropic.

1.4.4 Evaluation of entropy changes

If the work involved in a reversible process is only P-V work,

$$\delta w_{rev} = PdV \text{ and } TdS = \delta q_{rev}.$$

Hence

$$\Delta E = TdS - P\,dV \tag{1.59}$$

Equation 1.59 is in terms of state functions only and is applicable to all changes of state reversible or irreversible.

Entropy changes for ideal gases are given the following equations in terms of molar heat capacity, pressure/ volume and temperature.

$$\Delta S = n\,C_v \ln (T_2/T_1) + n\,R\,ln\,(V_2/V_1) \tag{1.60}$$

$$\Delta S = n\,C_p \ln (T_2/T_1) - n\,R\,ln\,(P_2/P_1) \tag{1.61}$$

Entropy changes for phase transitions at constant pressure is given by

$$\Delta S = \Delta H/T \tag{1.62}$$

The variation of entropy with temperature at constant pressure is given in terms of molar heat capacity and temperature as

$$(\Delta S)_p = n\,C_p \ln T_2/T_1 \qquad (1.63)$$

and for constant volume process

$$(\Delta S)_v = n\,C_v \ln T_2/T_1 \qquad (1.64)$$

The ΔS thus depends on the ratio of temperatures and not on their actual magnitudes.

1.5 Equilibrium and Spontaneity

Entropy is the basic concept which predicts the direction of a spontaneous process. In the case of isolated systems entropy of the system and its surroundings are considered together. However, many reactions are carried out at constant temperature, pressure or volume and in the case of such non-isolated systems which may be open, or closed, a change in spontaneity may be predicted on the basis of two alternatives:

(i) by evaluating the

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{sur}}$$

Three possibilities arise $\Delta S_{\text{total}} > 0$ for spontaneous reactions; $\Delta S_{\text{total}} = 0$ for reversible or equilibrium processes and $\Delta S_{\text{total}} < 0$ for non-spontaneous reactions. It is possible that $\Delta S < 0$ but, $\Delta S_{\text{total}} > 0$.

(ii) The second approach is to consider the system alone and define the conditions of spontaneity and equilibrium.

When a closed system alone is in thermal equilibrium with its surroundings at temperature T is considered, the change in entropy of the system, $\Delta S = 0$ at equilibrium. When a reversible change occurs in the system, transfer of heat occurs between the system and its surroundings such that

$$\Delta S = q_{\text{rev}}/T \quad \text{or} \quad (\Delta S - q_{\text{rev}}/T) = 0$$

However for an irreversible change $(\Delta S - q/T) \geq 0$. If the process is carried out at constant volume and no work is done $(q = 0)$ then

$$\Delta S - (\Delta E/T) \geq 0 \text{ or } T\Delta S - \Delta E \geq 0 \text{ or } T\Delta S \geq \Delta E \qquad (1.65)$$

Considering the system alone in the absence of any change in the internal energy or volume, a spontaneous transformation results in an increase in entropy and hence entropy can be used as a criterion for spontaneity of transformation. If the temperature is kept constant, instead of the internal energy, the entropy change at equilibrium may not be zero. This may be explained with an example of liquid water and water vapour at equilibrium. They have different molar entropies and hence, ΔS is not zero. This is due to the fact that when water evaporates even at a constant temperature, the latent heat of vapourisation is absorbed leading to an increase in the entropy of the water vapour. The internal energy also increases on vaporisation.

Thus for the system at constant T and V, $(\mathrm{d}V = 0;\ \mathrm{d}T = 0)$ it may be written for an isothermal change

$$d(TS) - d(E) \geq 0 \text{ or} -d(E - TS) \geq 0 \text{ or } d(E - TS) \leq 0 \qquad (1.66)$$

The quantity $(E - TS)$ represents a difference between state functions and may be represented by a new state function A (German A = arbeit = work) called *Helmholtz free energy* or *Helmholtz function* or *work function* so that

$$A = (E - TS) \qquad (1.67)$$

For a spontaneous process at constant T and V,

$$\Delta A = \Delta E - T\Delta S \qquad (1.68)$$

and the change in work function $\Delta A < 0$, for a reversible process at equilibrium it is zero. The equation implies that of the total amount of energy in a system only a part of it ($\Delta E - T\Delta S$) is available for work as the energy equal to $T\Delta S$ is stored in a disorderly manner and hence not available for doing work.

For a thermodynamically reversible process taking place isothermally,

$$\Delta A = \Delta E - q_{rev} \qquad \text{(because } \Delta S = q_{rev}/T\text{)} \tag{1.69}$$

According to first law of thermodynamics $\Delta E = q_{rev} - w_{rev}$ or $-w_{rev} = \Delta E - q_{rev}$

Substituting ΔA for $(\Delta E - q_{rev})$

$$\Delta A = -w_{rev} \quad \text{or} \quad w_{max} = -\Delta A \tag{1.70}$$

The decrease in the work function is equal to the maximum work that can be extracted from a system for an isothermal change between two states (at constant T and V). However, the work function is not used as a criterion of spontaneity because most transformations do not occur at constant volume.

For a system undergoing change at constant temperature and constant pressure ($dT = 0$, $dP = 0$) it can be written that

$$d(H - TS) \le 0 \tag{1.71}$$

The difference between the two state functions is represented by another state function G called *Gibbs free energy* or *free energy* given as

$$G = H - TS \tag{1.72 a}$$

$$= E + PV - TS \tag{1.72 b}$$

For a system undergoing spontaneous (irreversible) change at constant temperature and pressure $\Delta G < 0$. For changes under isothermal and isobaric conditions and for reversible changes $\Delta G = 0$. Since most chemical transformations occur at constant temperature and pressure, spontaneity of the process can be determined using the change in free energy as a criterion.

$$\Delta G = \Delta H - T\Delta S \tag{1.73}$$

Since $\Delta H = \Delta E + P\Delta V$ we can write

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad \text{or} \quad \Delta G = \Delta A + P\Delta V \tag{1.74}$$

Since $-\Delta A = w_{max}$

$$-\Delta G = w_{max} - P\Delta V \tag{1.75}$$

It is clear that the decrease in free energy at constant temperature and pressure corresponds to the maximum work other than *P-V* work (expansion work) that can be performed by a system under reversible conditions.

The free energy depends on T and P and hence is conveniently expressed in terms of T and P as independent variables.

$$dG = (\partial G/\partial P)_T\, dP + (\partial G/\partial T)_p\, dT \tag{1.76 a}$$

Complete differentiation of Eq. 1.72 a gives

$$dG = dH - TdS - SdT \tag{1.76 b}$$

But $TdS = dE + PdV$ (from Eq. 1.59) holds good for both reversible and irreversible processes. Further from Eq. 1.72 b H = E + PV and hence $dH = dE + PdV + VdP$. Substituting these into Eq. 1.76 b gives

$$dG = dE + PdV + VdP - dE - PdV - SdT$$

$$= VdP - SdT \tag{1.77}$$

Comparison of Eqs. 1.76 a and 1.77 shows that

$$(\partial G/\partial T)_p = -S \tag{1.78}$$

and $$(\partial G/\partial P)_T = V \tag{1.79}$$

From the above equations it is clear that G must increase with pressure at constant temperature and decrease with temperature at constant pressure. At constant temperature (isothermal change) $dT = 0$ and hence Eq. 1.77 becomes $dG = VdP$. The change in the free energy at constant temperature is obtained by integrating Eq. 1.79 between the initial and final pressures P_1 and P_2

$$\int_1^2 dG = \int_1^2 V.dP \tag{1.80}$$

In the case of solids and liquids V can be considered to be constant as they are only slightly compressible.

$$\int_1^2 dG = \mathrm{V}\int_1^2 dP \text{ or } \Delta G = V\Delta P = V(P_2 - P_1) \tag{1.81}$$

Free energy of pure solids and liquids are fairly constant over a wide range of pressures and hence changes in free energies are quite small. However, in the case of gases volume changes are quite appreciable with changes in pressures and hence changes in free energies are quite appreciable. For n mols of an ideal gas $V = n\,(\mathrm{R}T/P)$ hence

$$\Delta G = n\mathrm{R}T \ln(P_2/P_1) = n\mathrm{R}T \ln(V_1/V_2) \tag{1.82}$$

where V_1 and V_2 are the initial and final volumes respectively.

1.5.1 Standard free energies

Free energy G being a state function, only the changes in the free energy ΔG are thermodynamically significant and can be manipulated by way of addition or subtraction in a manner similar to ΔH. The free energy change of chemical reactions ΔG is more important than the changes in work function ΔA because most of the reactions are carried out at constant pressure (usually one atmospheric pressure).

The element in its stablest form at one atmospheric pressure at a specified temperature, usually 298 K, is considered to be in its standard state and the free energy G^0_{f298} of the element in its standard state is assumed to be zero. The standard free energy of formation of a compound is defined as the free energy change accompanying the formation of a compound from the constituent elements, the reactants and products being in their respective standard states at a specified temperature. The standard free energy change of a reaction can be calculated from a knowledge of the ΔG^0_f values of the reactants and products.

Thus the free energy change of formation of a compound at constant temperature = (total molar free energy of the products – total molar free energy of the reactants).

$$\Delta G^0_f = \Sigma G^0_f \text{ (products)} - \Sigma G^0_f \text{ (reactants)} \tag{1.83}$$

It is possible to predict whether a given transformation is feasible or not under standard conditions on the basis of the sign of ΔG^0_f. When ΔG^0_f is < 0 it is indicative of a spontaneous reaction and conversely the reaction is non-spontaneous when $\Delta G^0_f > 0$ and $\Delta G^0_f = 0$ at equilibrium.

The criteria for a chemical reaction to occur spontaneously may be summarized as ΔG should be negative at a given temperature and pressure with both ΔH and ΔS making significant contributions. For ΔG to be negative ΔH must be negative and ΔS must be positive. In the case of exothermic reactions

ΔH will be negative and $\Delta G \sim \Delta H$ and ΔS may be positive indicating spontaneity. However if the ΔS is negative the condition $|\Delta H| > |T\Delta S|$ should be satisfied for spontaneity. In the case of endothermic reactions ΔH and ΔS will be positive but ΔG will be negative only when $T\Delta S > \Delta H$.

1.5.2 Gibbs-Helmholtz equation

One can predict the feasibility of a chemical reaction only (298 K from the ΔG_f^0 values). Gibbs-Helmholtz equation is useful for predicting the feasibility of a reaction at other temperatures as it relates the variation of ΔG with temperature. The equation $\Delta G = \Delta H - T\Delta S$ (Eq. 1.73) itself is a simple form of Gibbs-Helmholtz equation. It states that ΔG is a function of T at constant pressure. Differentiating the above with respect to T

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \left(\frac{\partial(\Delta H)}{\partial T}\right)_P - T\left(\frac{\partial(\Delta S)}{\partial T}\right)_P - \Delta S\left(\frac{\partial T}{\partial T}\right)_P$$

$$= \left(\frac{\partial(\Delta H)}{\partial T}\right)_P - T\left(\frac{\partial(\Delta S)}{\partial T}\right)_P - \Delta S \tag{1.84}$$

Since $\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -\Delta S$

Substituting into Eq. 1.73 gives

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \tag{1.85}$$

Equation 1.85 is another form of Gibbs-Helmholtz equation.

Gibbs-Helmholtz equation can also be written in yet another form by differentiating $\Delta G/T$ with respect to T to arrive at

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \tag{1.86}$$

This is yet another way of representing the variation of ΔG with T.

1.6 Third Law of Thermodynamics

It was shown that as temperature decreases ΔG approaches ΔH and at extremely low temperatures near absolute zero $\Delta G = \Delta H$. Nernst suggested that ΔG and ΔH approach equality asymptotically at temperatures close to absolute zero. Nernst heat theorem postulates that *in the neighbourhood of absolute zero, all processes should occur without any change in the entropy and heat capacity*. The entropy of a substance at any temperature must be greater than its value at absolute zero as S = 0 at $T \to 0$.

Planck extended Nernst's assumption by stating that *the value of the entropy of a pure solid or a pure liquid approaches zero at absolute zero.*

$$S_T - S_0 = \int_0^T \frac{C_P}{T} \mathrm{d}T \tag{1.87}$$

Lewis and Randall stated the third law of thermodynamics as *every substance, element or compound has a finite positive entropy, but at the absolute zero of temperature, the entropy may become zero and does become so in the case of a perfectly crystalline substance.* Eq. 1.87 may be written as

$$S_T = \int_0^T C_P\, d\,(\ln T) \quad \text{or} \quad S_T = \int_0^T \frac{C_P}{T} dT \tag{1.88}$$

S_T in the above equation is called the third law entropy or absolute entropy. If the pressure is one atm., then the entropy is also the standard entropy S^0. The third law places a limitation on the value of entropy and also leads to the important conclusion of the impossibility of attaining absolute zero.

1.7 Thermodynamic Applications to Physical Equilibria

For any pure substance in single phase of gas, liquid or solid, any variation in free energy is given by the Eq. 1.77 as $dG = VdP - SdT$. To have equilibrium in the phase, dG must be zero at constant T and P and the phase is said to be in equilibrium when the pressure and temperature are constant and uniform throughout the phase.

For any pure substance undergoing change from one phase to another as in the case of one crystalline form changing to another crystalline form or melting of a solid or vapourisation of a liquid, the change in free energy for phase transition can be represented as

$$\Delta G = G_2 - G_1 \tag{1.89}$$

where G_1 and G_2 are the molar free energies of the substance in the initial and final states respectively. If the two phases of the substance are in equilibrium and the pressure of the system is changed by dP, then the temperature of the system will have to change by dT in order to preserve the equilibrium. Since at equilibrium $G_1 = G_2$ and also $dG_1 = dG_1$. But by Eq. 1.77, $dG_1 = V_1dP - S_1dT$ and $dG_2 = V_2dP - S_2dT$. Equating these expressions gives

$$V_2dP - S_2dT = V_1\, dP - S_1dT$$

$$(V_2 - V_1)\, dP = (S_2 - S_1)\, dT$$

$$dP/dT = \Delta S/\Delta V \tag{1.90}$$

where $\Delta S = (S_2 - S_1)$ the change in entropy and $\Delta V = (V_2 - V_1)$ the change in volume for the process. The Eq. 1.90 is known as ***Clayperon equation***. Since phase changes are reversible isothermal processes $\Delta S = \Delta H/T$ (Eq. 1.62) where ΔH is the heat absorbed or enthalpy change per mol at the temperature T and is usually called the latent heat, L. For the phase transition solid to liquid $\Delta H = L_f$ (latent heat of fusion) and similarly for the transition liquid to vapour $\Delta H = L_v$ (latent heat of vapourization)

Equation 1.90 can be written as

$$dP/dT = L/T\Delta V \tag{1.91}$$

In the case of phase transition solid to liquid $\Delta V = V_l - V_s$ and for liquid to vapour $\Delta V = V_g - V_l$ where V_s, V_l and V_g are the molar volumes of the solid, liquid and vapour respectively. The more useful ***Clausius-Clayperon Equation*** (1.92) for calculating the latent heat of phase transformation is based on the following assumptions for liquid-vapour equilibrium (vapourisation) and solid-vapour equilibrium (sublimation).

$$\Delta V = V_g - V_l \sim V_g \text{ since } (V_g >> V_l) \text{ and } \Delta V = V_g - V_s \sim V_g \text{ since } (V_g >> V_s)$$

Assuming that the vapour behaves as an ideal gas $V_g = RT/P$, Eq. 1.91 becomes

$$dP/dT = L/TV_g$$

$$dP/dT = L\,P/RT^2$$

$$1/P\,(\mathrm{d}P/\mathrm{d}T) = L/RT^2$$

or
$$\mathrm{d}\ln P/\mathrm{d}T = L/RT^2 \qquad (1.92)$$

Assuming that L remains constant over a small temperature change and integrating the above equation gives

$$\ln P_2/P_1 = L/R\,[(T_2 - T_1)/T_1T_2)] \qquad (1.93)$$

where P_1 and P_2 are the vapour pressures at T_1 and T_2 respectively. It is possible to calculate the latent heat of transformation by using the above equation.

1.8 Thermodynamic Applications to Chemical Equilibria

1.8.1 Partial molar free energy (Chemical Potential)

The derivations of various thermodynamic equations presented so far were based on the consideration of *closed systems* only as any change of state of the system was assumed to be due to changes in temperature or pressure. However in the case of *open systems*, the state functions change due to change in mass and composition also. Thermodynamic properties such as E, H, S, G, A, etc., are extensive properties because they depend not only P, V and T but also on the mass or number of mols, n of each constituent and composition of the mixture. The change in free energy dG, the most useful state function in chemistry, at constant T and P may be given in terms of the *partial molar free energy* $\bar{G}_i$ and the number of mols of the component n as

$$(\mathrm{d}G)_{T,P} = \textstyle\sum_i \bar{G}_i\,\mathrm{d}n_i \qquad (1.94)$$

However if the temperature and pressure are not constant Eq. 1.77 becomes

$$(\mathrm{d}G)_{T,P} = V\mathrm{d}P - S\mathrm{d}T + \textstyle\sum_i \bar{G}_i\,dn_i \qquad (1.95)$$

Gibbs called the *partial molar free energy* as ***chemical potential*** represented as μ

$$(\partial G/\partial n_i)_{T,P,ni} = \bar{G}_i = \mu_i \qquad (1.96)$$

and hence Eq. 1.95 may be written as

$$(\mathrm{d}G)_{T,P} = V\mathrm{d}P - S\mathrm{d}T + \textstyle\sum_i \mu_i\,\mathrm{d}\,n_i \qquad (1.97)$$

where the summation includes all the i constituents of the mixture. When small amount of substance i (dn_i moles) is added to the system keeping all other variables constant, the change in free energy of the system is related to the composition of the system as given by

$$(\mathrm{d}G)_{T,P} = \textstyle\sum_i \mu_i\,d\,n_i. \qquad (1.98)$$

The Eq. 1.98 is called *Gibbs-Duhem* equation. Other forms of Gibbs-Duhem Equation include

$$G = \textstyle\sum_i \mu_i\,n_i\ ;\ \sum_i n_i\,d\mu_i = 0 \qquad (1.99\text{ a})$$

The chemical potential of each constituent is the contribution per mol of that constituent of the mixture towards the total free energy of the system at constant temperature and pressure. It is an intensive property of the system as it does not depend on the amount of the material but only its composition at constant temperature and pressure. For one mol of a pure substance (one-component system) the chemical potential is equal to the molar free energy ($\mu = G/n$). The chemical potential is considered as the driving force behind a change. The concept of partial molar properties is useful to determine the properties of non-ideal mixtures. For example the total volume of a solution of two components V will be equal to the sum of the individual volumes V_A and V_B only if the A and B form an ideal solution. In general $V \neq V_A + V_B$. The increase in volume of the solution is calculated from the values of partial molar volumes and the number of mols of the components using the relationship

$$dV = \bar{V}_A n_A + \bar{V}_B n_B \qquad (1.99\text{ b})$$

The variation of chemical potential of a component of a system as a function of temperature is related to *partial molar entropy* $\bar{S}_i$ of the component as given by

$$(\partial\mu_i/\partial T)_{P,\,ni} = -\bar{S}_i \qquad (1.100)$$

Since the entropy of a substance is always positive, the chemical potential would decrease with increase in temperature as given by the above equation. The variation of chemical potential as a function of temperature for solids, liquids and gases is shown in Figure 1.1.

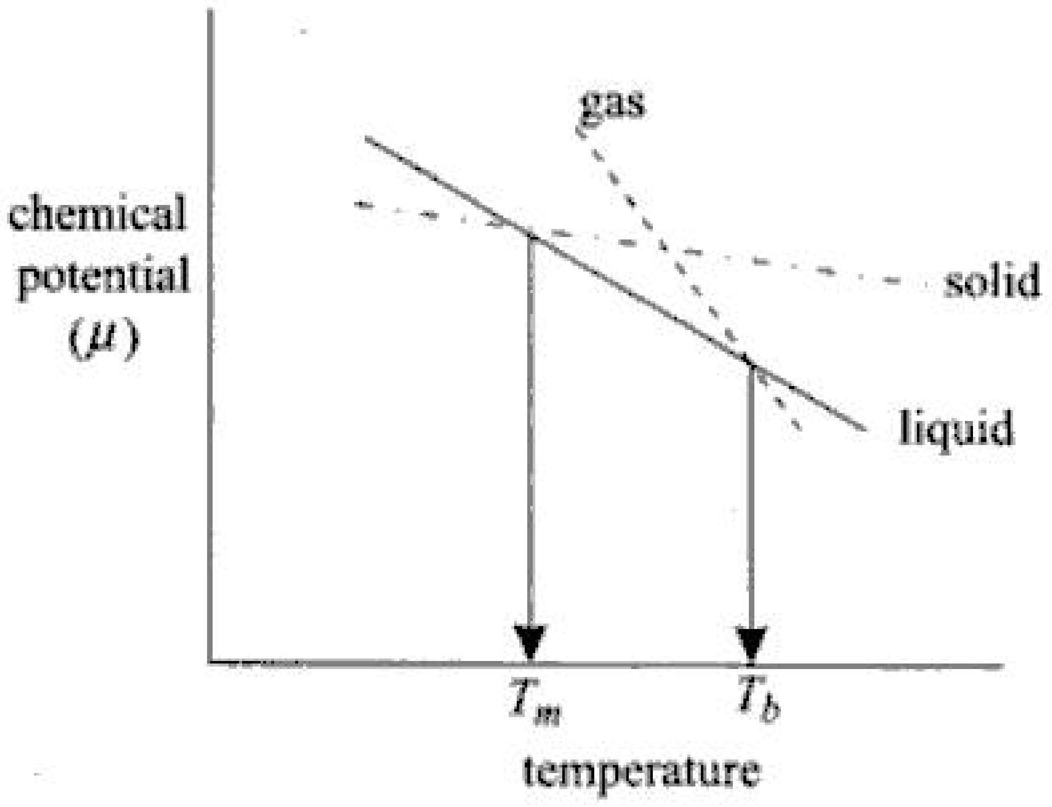


Fig. 1.1 Variation of chemical potential with temperature

The chemical potentials of the solid and liquid phases of a substance are the same at the melting temperature T_m and similarly the chemical potentials of the liquid and vapour phases remain the same at the boiling temperature T_b.

Similarly the variation of the chemical potential of a component i of a system with pressure is related to the *partial molar volume* V_i of the component as given by

$$(\partial\mu_i/\partial P)_{T,\,ni} = -\bar{V}_i \qquad (1.101)$$

1.8.2 Van't Hoff reaction isotherm and Van't Hoff equations

Many chemical reactions do not go to a completion and may be considered as reversible reactions or equilibrium reactions. Chemical equilibria are dynamic and the rates of the forward and reverse reactions are the same at equilibrium. Chemical equilibria are also affected by changes in temperature, pressure and concentration of reactants. Guldberg and Waage proposed the law of mass action based on the effect of concentration on the rates of chemical reactions as 'at a constant temperature, the velocity of a chemical reaction is proportional to the *active masses* of the reacting substances.' Guldberg and Waage assumed that active mass is equal to the partial pressures of the gases and concentration (expressed in mol/liter) in solutions. According to the law of mass action for a chemical equilibrium represented by

$$\mathrm{aA + bB \rightleftharpoons cC + dD} \qquad (1.102)$$

the rate of the forward and reverse reactions v_f and v_r are given respectively by

$$v_f = k_f[\mathrm{A}]^a[\mathrm{B}]^b \quad \text{and} \quad v_r = k_r[\mathrm{C}]^c[\mathrm{D}]^d \tag{1.103}$$

where k_f and k_r represent proportionality constants for the forward and reverse reactions and concentrations of the reactants and products are represented within square brackets. At equilibrium $v_f = v_r$ and

$$\frac{k_f}{k_r} = K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \tag{1.104}$$

The ratio k_f / k_r is called the equilibrium constant K a constant at a given temperature. The equilibrium constant is also given as the ratio of the product of the concentrations of the products at equilibrium raised to powers corresponding to the appropriate stoichiometric coefficients, to the concentration of the reactants remaining at equilibrium raised to powers corresponding to their appropriate stoichiometric coefficients. Thus the equilibrium constant is governed by the ratio of the concentrations of the products to that of the reactants at a given temperature and is independent of the initial concentrations of the reactants.

Thermodynamic derivation of the expression for equilibrium constant is based on the condition that the free energy change accompanying the reaction at equilibrium must be equal to zero. The system at equilibrium is composed of several substances with varying compositions and hence the thermodynamic properties of the system must be expressed in terms of partial molar quantities The *partial molar free energy*, also called *chemical potential* μ is related to dG at constant T and P by the Gibbs-Duhem Equation (1.98).

The chemical potential of any constituent in any state may be expressed in terms of its activity a in that state as

$$\mu = \mu^0 + RT \ln a \tag{1.105}$$

where μ^0 is called the standard chemical potential or chemical potential in the standard state of unit activity.

The system at equilibrium may be considered as *dn* mol of each reactant gives rise to *dn* moles of each product. The concentrations of the reactants A and B diminish by *a dn* and *b dn* moles respectively while the concentrations of the products C and D increase by *c dn* and *d dn* moles respectively. The free energy change dG accompanying the process is given in terms of chemical potentials and may be written as chemical potential of the products – chemical potential of the reactants and represented based on Eq. 1.98 as

$$(dG)_{T,P} = \sum \mu\, dn = (\mu_C\, c\, dn + \mu_D\, d\, dn) - (\mu_A\, a\, dn + \mu_B\, b\, dn) \tag{1.106}$$

At equilibrium $(\mathrm{d}G)_{T,P} = 0$. Substituting for μ in terms of μ^0 and activities

$$\Delta G = 0 = [c\,(\mu_C^0 + RT \ln a_C) + d\,(\mu_D^0 + RT \ln a_D)] - [a\,(\mu_A^0 + RT \ln a_A) + b\,(\mu_B^0 + RT \ln a_B)] \tag{1.107}$$

$$= [(c\,\mu_C^0 + d\,\mu_D^0) - (a\,\mu_A^0 + b\,\mu_B^0)] + RT \ln\left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right) \tag{1.108}$$

$$\Delta G = 0 = \Delta G^0 + RT \ln\left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right) \tag{1.109}$$

or
$$-(\Delta G^0/RT) = \ln\left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right) \tag{1.110}$$

The left-hand side of the above equation is a constant. The ratio of the activities of the products and the reactants is also a constant at equilibrium for a given temperature and pressure and taking the term as equal to K, it may be written as

$$\Delta G^0 = -RT\ln K \text{ or } K = \exp\left(-(\Delta G^0/RT)\right) \tag{1.111}$$

where K is a thermodynamic equilibrium constant. The above relation holds good for all reversible reactions of all types involving gases, liquids and solids. In general the change in the free energy accompanying a reaction (Eq. 1.110) may be given as

$$\Delta G = \Delta G^0 + RT\ln Q \tag{1.112 a}$$

$$= -RT\ln K + RT\ln Q \tag{1.112 b}$$

The equation is called the *van't Hoff reaction isotherm*. The thermodynamic equilibrium constant K is the ratio of the activities of the products and the reactants at equilibrium while Q (called reaction quotient) is the ratio of the activities of the products and the reactants at any state of the reaction. When $\Delta G = 0$, $\Delta G^0 = -RT\ln Q$ and Q becomes K, the activities correspond to equilibrium activities.

The activities depend on the chosen standard state in which the reaction takes place. For reactions involving gases the standard state chosen is that of the ideal gas at one atm. pressure and the activity of the gas is related to its partial pressure. The equilibrium constant is expressed in terms of partial pressures and given the symbol K_p. In the case of liquid phase reactions, the standard state is chosen as the ideal solution of unit concentration (molarity or molality) and activities are related to molar concentrations. The equilibrium constant is expressed in terms of molar concentrations and given the symbol K_c. Writing the Eq. 1.112 b as

$$\Delta G = RT\ln Q/K \tag{1.113}$$

it can be seen that ΔG depends only the ratio Q/K as long as both are referred to the same standard state and independent of the particular standard state chosen.

Van't Hoff reaction isotherm is useful in determining the feasibility of a reaction under a given set of conditions. Only when $Q < K$, $\Delta G < 0$ and the reaction is spontaneous and when $Q > K$, $\Delta G > 0$ and the reaction is not feasible under the chosen conditions of temperature, pressure or concentrations. However, the value of K may increase with temperature and at some temperature $K > Q$.

The variation of the equilibrium constant K with temperature is expressed by *van't Hoff equations*. For reactions carried out at constant pressure the equation may be obtained by combining Eq. 1.111 and Gibbs-Helmholtz Equation (1.86).

$$\Delta G^0 = -RT\ln K \text{ or } \ln K = -\Delta G^0/RT \qquad \text{(Eq. 1.111)}$$

Differentiating the above equation with respect to T

$$\frac{\partial \ln K}{\partial T} = -\frac{1}{R}\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{1}{R}\left(\frac{-\Delta H^0}{T^2}\right) \tag{1.114}$$

ΔH^0 represents the standard enthalpy change accompanying the reaction. Since ΔH does not vary much with pressure ΔH is taken to be approximately equal to ΔH^0. Hence

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \tag{1.115}$$

The equation is known as *van't Hoff equation*. On integrating the above equation another more useful form of the equation is obtained.

$$\ln K = -\frac{\Delta H}{RT} + \text{constant or } \log K = -\frac{\Delta H}{2.303\,RT} + \text{constant} \qquad (1.116)$$

A plot of log K against $1/T$ gives a straight line with a slope of $-(\Delta H/2.303R)$. If the integration is carried out assuming ΔH to be constant between the temperatures T_1 and T_2 it is possible to calculate the equilibrium constant at T_2 if K is known at T_1 using the Eq. 1.106 which is yet another form of van't Hoff equation.

$$\log (K_2/K_1) = -(\Delta H/2.303\,R)\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad (1.117)$$

A similar equation called *van't Hoff isochore* is obtained for reactions carried out at constant volume.

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta E}{RT^2} \qquad (1.118)$$

1.9 Maxwell Relations

Maxwell relations are mathematical expressions relating the different thermodynamic properties of a system to easily measurable physical quantities such as P, T, V, etc. Maxwell relations are useful for interpreting physical properties of substances. Table 1.1 gives the various Maxwell relationships derived from the differential forms of fundamental thermodynamic expressions.

Table 1.1 Maxwell relations

Thermodynamic functions	*Differential equations*	*Independent variables*	*Maxwell relations*	
E	$dE = TdS - PdV$	S and V	$(\partial T/\partial V)_S = -(\partial P/\partial S)_V$	**(A)**
H	$dH = TdS + VdP$	S and P	$(\partial T/\partial P)_S = (\partial V/\partial S)_P$	**(B)**
A	$dA = -SdT - PdV$	T and V	$\partial S/\partial V)_T = (\partial P/\partial T)_V$	**(C)**
G	$dG = -SdT + VdP$	T and P	$(\partial V/\partial T)_P = -(\partial S/\partial P)_T$	**(D)**

The expressions may be derived as follows:

1. Based on first and second laws $dE = T\,dS - PdV$ (Eq. 1.59)

   Since E is a function of S and V the total differential equation for dE is written as

   $$dE = (\partial E/\partial S)_v\, dS + (\partial E/\partial V)_S\, dV \qquad (1.119)$$

   On comparing the above two equations. we get

   $$(\partial E/\partial S)_v = T \qquad (1.120\text{ a})$$

   and $$(\partial E/\partial V)_S = -P \qquad (1.120\text{ b})$$

   Differentiating the Eq. 1.120 a with respect to V at constant S gives

   $$(\partial/\partial V)\,[(\partial E/\partial S)_v\,]_S = (\partial T/\partial V)_s \qquad (1.121\text{ a})$$

and similarly differentiating Eq. 1.120 b with respect to S at constant V gives

$$(\partial/\partial S)\,[(\partial E/\partial V)_s]_v = -\,(\partial P/\partial S)_v \tag{1.121 b}$$

But the left-hand sides of the above two equations are equal as E is a state function.

Hence

$$(\partial T/\partial V)_s = -\,(\partial P/\partial S)_v \tag{A}$$

2. Maxwell's second relationship is obtained in a similar manner. Since $H = E + PV$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \tag{1.122}$$

Since H is a function of S and P the total differential equation for $\mathrm{d}H$ is

$$\mathrm{d}H = (\partial H/\partial S)_P\,\mathrm{d}S + (\partial H/\partial P)_S\,\mathrm{d}P \tag{1.123}$$

Comparing the Eqs. 1.122 and 1.123 gives

$$(\partial H/\partial S)_P = T \tag{1.124 a}$$

and

$$(\partial H/\partial P)_s = V \tag{1.124 b}$$

Differentiating Eq. 1.124 a with respect to P at constant S gives

$$(\partial/\partial P)\,[(\partial H/\partial S)_P\,]_S = (\partial T/\partial P)_s \tag{1.125 a}$$

and on differentiating Eq. 1.124 b with respect to S at constant P gives

$$(\partial/\partial S)\,[(\partial H/\partial P)_S\,]_P = (\partial V/\partial S)_P \tag{1.125 b}$$

Since H is a state function and $\mathrm{d}H$ is an exact differential hence

$$[\partial^2 H/(\partial S\,\partial P)] = [\partial^2 H/(\partial P\,\partial S)]$$

Comparing Eqs. 1.125 a and 1.125 b we get the second relationship of Maxwell as

$$(\partial T/\partial P)_s = (\partial V/\partial S)_P \tag{B}$$

3. Maxwell's third equation (C) is obtained from the variables T and V as follows:

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V$$

At constant V

$$(\partial A/\partial T)_v = -\,S \tag{1.126 a}$$

and at constant T

$$(\partial A/\partial V)_T = -\,P \tag{1.126 b}$$

Differentiating equation (1.126 a) with respect to V at constant T gives

$$(\partial/\partial V)\,[(\partial A/\partial T)_v]_T = -\,(\partial S/\partial V)_T$$

Differentiating equation (1.126 b) with respect to T at constant V gives

$$(\partial/\partial T)\,[(\partial A/\partial V)_T]_V = -\,(\partial P/\partial T)_v \tag{1.127 a}$$

Since A is a point function the order of differentiation does not affect its properties. Hence the above second derivatives are equal.

$$(\partial/\partial V)\,[(\partial A/\partial T)_v] = (\partial/\partial T)\,[(\partial A/\partial V)_T] \tag{1.127 b}$$

Therefore

$$(\partial S/\partial V)_T = (\partial P/\partial T)_v \tag{C}$$

4. Equation 1.77 is $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$

At constant temperature $\mathrm{d}T = 0$ hence

$$(\mathrm{d}G)_T = V(\mathrm{d}P)_T \text{ or } (\partial G/\partial P)_T = V \tag{1.128 a}$$

At constant pressure $\mathrm{d}P = 0$ and Eq. 1.77 simplifies to

$$(\mathrm{d}G)_P = -\,S(\mathrm{d}T)_P \text{ or } (\partial G/\partial T)_P = -\,S \tag{1.128 b}$$

On differentiating Eq. 1.128 a with respect to T at constant P gives

$$(\partial/\partial T)\,[(\partial G/\partial P)_T]_P = (\partial V/\partial T)_P \tag{1.129 a}$$

Similarly differentiating Eq. 1.128 b with respect to P at constant T gives

$$(\partial/\partial P)\,[(\partial G/\partial T)_P]_T = -\,(\partial S/\partial P)_T \qquad (1.129\ \text{b})$$

G is a state function and dG is an exact differential and hence Maxwell's relation is

$$(\partial V/\partial T)_P = -\,(\partial S/\partial P)_T \qquad \textbf{(D)}$$

Solved Examples

1. Calculate the (a) work done by 2.5 moles of a gas under isothermal conditions at 30° C when it expands from 10 liters to 50 liters against an external pressure of 1 atm. and when it expands reversibly.

Solution:

(a) $w = PdV$ = 1 atm. pr. × 101.3 j (40 l) = **4052 j**

(b) $w = nRT \ln (V_2/V_1)$

= 2.5 mols × 8.314 j/deg/moles × (303 K) × (ln 50/10)

= **10135.76 J or 10.135 kJ**

◆

2. Calculate w, q and ΔE for 2 mols of an ideal gas expanding from 10 atm to 1 atm. reversibly under isothermal conditions (T = 25° C).

Solution:

$w = n\,RT \ln (P_1/P_2)$ and since $\Delta E = 0$, $q = w$)

= 2 × 8.314 × 298 × ln (10/1)

= 11,411.7 J = **11.41 kJ**

q = **11.41 kJ**

◆

3. Calculate ΔE for the combustion of liquid benzene if the heat of reaction at constant pressure at 25° C was determined to be – 780.98 k.cal/mol.

Solution:

$C_6H_6(l) + 7\tfrac{1}{2}O_2 \longrightarrow 6\,CO_2(g) + 3\,H_2O\,(l)$;

ΔH = 780.98 k.cal $\qquad \Delta E = \Delta H - \Delta n\,RT$

= – 780.98 k.cal – [(–1.5)×1.99 ×10^{-3} k.cal.× 298]

= –780.98 + 0.889 = **– 780.09 k.cal/mol**

◆

4. Calculate the ΔE for the oxidation 1 mol of hydrogen to yield 1 mol of liquid water, if the standard heat of formation of water is – 285.85 kJ/mol.

Solution:

$H_2(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)$

$\Delta E = \Delta H - \Delta n\,RT$

= – 285.85 k.J – [(–1 ½) × 8.314 × 10^{-3} kJ × 298)]

= – 285.85 + 3.716 = **– 282.13kJ/mol**

◆

5. Calculate the enthalpy change when 50 g of water is heated from 30° C to 45° C at one atmospheric pressure. Assume the molar heat capacity remains constant in the temperature range at 18.1 cal/K/mol.

Solution:

$\Delta H = nC_p(T_2 - T_1)$

= (50/18) × 18.1 cal/K/mol × (343 – 328)

= 2.78 × 18.1 × 15 = **754.8 cal/mol**

◆

6. Calculate the heat of formation of water at 100° C, if the standard heat of formation of water vapour is – 241.83 kJ and the molar heat capacities of hydrogen, oxygen and water vapour are assumed to remain the same in the temperature range at 29.0, 29.16 and 36.4 J/deg mol.

Solution: Enthalpies at two different temperatures are related to the difference in mean molar heat capacities of products and reactants

($\Delta C_p = C_p$ (products) – C_p (reactants))

as given by the equation

ΔH (at T_2) – ΔH (at T_1) = $\Delta C_p\,(T_2 - T_1)$.

$H_2(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g)$; ΔH_f^0

(at 298 K) = –241.83 kJ

ΔC_p = 36.4 – (29.0 + ½ × 29.16)

= –7.18 × 10^{-3} kJ/deg

ΔH_f^0 (at 373 K) = ΔH_f^0 (at 298 K) + ΔC_p (373–298)

= – 241.83 + (– 7.18×10^{-3} × 75)

= **– 242.37 kJ/mol**

◆

7. Calculate the standard heat of formation ΔH_f^0 of propane from its elements if ΔH for combustion of propane is – 530.6 k.cal/mol at 25° C and ΔH_f^0 for CO_2 and H_2O (l) are – 94.05 and – 68.32 kcal respectively.

Solution:

$C_3H_8(g) + 5O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O\,(l)$;

$\Delta H = -530.6$ k.cal

ΔH_f^0 (propane) = [3 (ΔH_f^0 (CO_2) + 4 ΔH_f^0 (H_2O)] − ΔH(combustion)

= [3 (− 94.05) + 4 (−68.32)] − (−530.6)

= − 555.43 + 530.6 = **− 24.83 k.cal/mol**

◆

8. Calculate the enthalpy of change at 25° C for the reaction

$$H_2C = CH_2(g) + H_2(g) \longrightarrow C_2H_6$$

from the available bond enthalpy (energy) data of H−H = 104 k.cal, C−C = 83 k.cal, C−H = 99 k.cal and C=C = 147 k.cal.

Solution:

$\Delta H = -(\Delta H_{C-C} + 2\Delta H_{C-H}) + (\Delta H_{C=C} + \Delta H_{H-H})$

= − (83 + 98) + (147+104) = **− 30 k.cal**

◆

9. Calculate the heat of formation of CO at constant pressure if the heat of formation at constant volume at 30° C is 28.6 k.cal/mol.

Solution:

$C(s) + \frac{1}{2}O_2 \longrightarrow CO\,(g)$:

ΔE = 28.6 k.cal ; Δn = 1 − 1/2 = 1/2

$\Delta H = \Delta E + \Delta n\, RT$

= 28.6 × 10³ cal × ½ × 1.99 × 303

= **288.98 k.cal/mol**

◆

10. The free energy change Δ*G* for a reaction is found to be −3.138 k.cal at 300 K and $(\partial\,(\Delta G)/\partial\,T)$ is −14.39 cal/deg. Find ΔH for the reaction at 300 K.

Solution:

From Gibbs-Helmholtz equation

$$\Delta H = \Delta G - T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

= − 3138 − 300 (−14.39)

= − 3138 + 4317 = + 1179 cal = **+ 1.179 k.cal**

◆

11. The equilibrium constant for the reaction

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

is 1.64 × 10⁻⁴ atm. at 400°C and 0.144 × 10⁻⁴ at 500° C respectively. Calculate the heat of formation of 1 mol of ammonia from its elements within the given temperature range.

Solution:

$$\log (K_2/K_1) = -(\Delta H / 2.303\ R)\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log \frac{1.64\times10^{-4}}{0.144\times10^{-4}} = -[\Delta H/(2.303 \times 8.314)]$$

(100/673 × 773)

$1.0565 = -\Delta H/(19.147) \times 1.922 \times 10^{-4}$

ΔH = − 105.25 kJ/2 mol or **− 52.6 kJ/mol**

◆

12. Equilibrium constant for a reaction is 10,000 at 25° C. Calculate ΔG for the reaction.

Solution:

$\Delta G = -RT \ln K$

= − 1.99 × 298 × ln 10,000

= **− 5461.7 cal**

◆

13. Calculate the entropy increase in the evaporation of one mol of water at 100° C. The latent heat of vaporisation of water at 100° C is 540 cal/g.

Solution:

Since latent heat of vapourization

$= q_{rev}$ = 540 cal/g × 18 g/mol = 9720 cal/mol

$\Delta S = q_{rev} / T$ = 9720/373 = **26.06 cal/mol/K**

◆

14. Gibbs free energy change for a reaction at 300 K and 310 K are −29.k.cal and −29.5 k.cal respectively. Determine Δ*H* and Δ*S* at 300 K.

Solution:

$\Delta S = [\partial\,\Delta G/\partial T]$

$$= \frac{\Delta G_{310} - \Delta G_{300}}{T_2 - T_1} = \frac{-29{,}500 + 29000}{10}$$

= **− 50 cal/deg**

$\Delta H = \Delta G + T\Delta S = -29{,}000 + (50 \times 300)$

= − 14,000cal = **−14.0 K.cal.**

◆

15. Calculate the entropy change when 100 g of solid ice is transformed to liquid water at 0° C and 1 atm. pressure. The latent heat of fusion is 79.92 cal/g.

Solution:

$\Delta S = \Delta H/T$ (since $q_{rev} = \Delta H$ at constant pressure and given temperature)

= (79.92 × 100)/273 = **29.27 cal/K**

◆

16. Calculate the entropy change when 5 mols of an ideal gas expands isothermally and reversibly to 3 times its initial volume.

Solution:

$$\Delta S = n\,C_v \ln (T_2/T_1) + n\,R \ln (V_2/V_1)$$
$$= 0 + 5 \times 8.3\ 14 \times \ln 2.5 = \mathbf{38.1\ J/K}$$

◆

17. Calculate ΔS when an ideal gas undergoes a change from its initial temperature of $-10°$ C at 5 atm.pressure to $-40°$ C and 1.5 atm. pressure. (For one mol of an ideal gas $C_v = 1.5$ R).

Solution:

$$\Delta S = n\,C_p \ln (T_2/T_1) - n\,R \ln (P_2/P_1)$$
$$C_p = C_v + R = 2.5R$$
$$= 5 \times 2.5 \times 8.314 \times \ln (233/263) - 5 \times 8.314 \times \ln (1.5/5)$$
$$= -12.575 - (-50.05) = \mathbf{37.475\ J/K/mol}$$

◆

Review Questions

1. Explain the terms system, surroundings and boundaries.
2. What are the different types of processes by which a system changes from one state to another.
3. Explain the term state function. Give examples.
4. Distinguish between extensive and intensive properties.
5. How is the absolute scale of temperature arrived at?
6. What are reversible and irreversible processes?
7. How are heat, work and energy related?
8. State the first law of thermodynamics and explain its significance.
9. What are the heat changes that occur in chemical systems?
10. What is the meaning of enthalpy? How is it expressed?
11. Explain the term molar heat capacity? How does it vary with pressure and temperature?
12. Write a note on the application of first law of thermodynamics to an ideal gas.
13. State Hess's law of constant heat summation. How is it useful?
14. What is bond energy?
15. What are the limitations of the first law of thermodynamics?
16. State the second law of thermodynamics and its significance.
17. Explain the term entropy. How does it change in reversible and irreversible processes?
18. State the thermodynamic criteria for spontaneous process at constant temperature and constant pressure.
19. What is work function? How is it related to entropy?
20. Derive the Gibbs-Helmholtz equation. What are its applications?
21. How is the entropy change expressed in terms of P and T of the system?
22. What is absolute entropy?
23. Derive the Clayperon and Clausius-Clayperon equations. What is their use?
24. Derive an expression for the variation of equilibrium constant of a reaction with temperature.
25. What are Maxwell relations? Derive any one relation.
26. Explain the term chemical potential. How does it vary with temperature and pressure?

2

PHASE RULE

2.1 Phase Equilibrium

Phase equilibrium is said to exist when two or more phases coexist in a heterogeneous system. Such a heterogeneous system is conveniently studied on the basis of thermodynamic considerations by a generalisation called *Phase rule* deduced by J. Willard Gibbs (1876). The effects of temperature, pressure and concentration of the constituents on the heterogeneous equilibrium may be predicted quantitatively with the help of a phase diagram.

2.2 Definitions

The terminology used in phase rule needs definition. Accordingly a ***phase*** is a homogeneous and physically distinct portion of a system separated from other parts of the system by definite boundaries. The phase can be separated by mechanical operations such as decantation, sedimentation, filtration etc., which are carried out without affecting the temperature, pressure or composition of the system. Separation methods such as evaporation, distillation, adsorption or extraction are not included as they interfere with the temperature, pressure or composition of the system. Phase rule is concerned with the existence or non-existence of a phase under a given set of conditions. Since gases are readily miscible in all proportions a mixture of gases such as air constitutes a single phase. In the case of liquids the number of phases present depends on the miscibility of the liquids. A liquid layer is considered as a single phase as long as it is homogeneous irrespective of whether it is a pure substance or a mixture of a number of miscible liquids. When two liquids are immiscible and a surface of separation exists between them the system consists of two phases. Each solid constitutes a separate phase. Each crystalline phase of a polymorphic solid or allotropic form of an element is a separate phase with distinct boundaries (e.g., rhombic sulphur and monoclinic sulphur). A solid solution on the other hand is homogeneous irrespective of the number of solids and hence constitutes a single phase.

Component of a system is an independent chemical constituent and the *number of components* of a system at equilibrium is the smallest number of independently variable chemical constituents by which the composition of each phase can be expressed directly or in the form of a chemical equation. For example the ice-water-water vapour system consists of three phases but all the phases can be represented by a single chemical component, namely, H_2O. Hence this system is a one-component system. In writing of chemical equations the use of +, – or 0 as coefficients is permissible. The number of components in a given system at equilibrium is also equal to the difference between the number of chemical species and the number of equations relating to the concentrations of these substances at equilibrium. Thus the decomposition of calcium carbonate as represented by the following equilibrium consists of three phases,

$$CaCO_3\,(s) = CaO\,(s) + CO_2\,(g) \tag{2.1}$$

solid $CaCO_3$, solid CaO and gaseous CO_2 but the number of components is only two because each of three phases can be described in terms of any of the two components as given by the following equations.

Phase	Components					
	CaO and CO_2	**or**	$CaCO_3$ and CaO	**or**	$CaCO_3$ and CO_2	
$CaCO_3 =$	$CaO + CO_2$	**or**	$CaCO_3 + 0\,CaO$	**or**	$CaCO_3 + 0\,CO_2$	(2.2)
$CaO =$	$CaO + 0\,CO_2$	**or**	$0\,CaCO_3 + CaO$	**or**	$CaCO_3 - CO_2$	(2.3)
$CO_2 =$	$0\,CaO + CO_2$	**or**	$CaCO_3 - CaO$	**or**	$0\,CaCO_3 + CO_2$	(2.4)

2.3 Gibbs' Phase Rule

The number of ***degrees of freedom***, F, is related to the number of phases P and the number of components C in a heterogeneous system existing in equilibrium. The relationship is expressed as given by 2.5 and is known as *phase rule*.

$$F = C - P + 2 \tag{2.5}$$

The term degrees of freedom or variance refers to the minimum number of independently variable factors, such as temperature, pressure and composition of phases that must be specified in order to describe the conditions of a system. For example when liquid water, solid ice and water vapour coexist in equilibrium the degrees of freedom $F = 0$ and the system is said to be invariant or non-variant as the three phases can coexist only at particular temperature and pressure which are automatically specified. When only two phases of the same system coexist the degree of freedom $F = 1$ and either temperature or pressure has to be specified.

2.4 Application of Phase Rule to One-Component Systems

One-component systems include the water system and the sulphur system. For a one-component system the degrees of freedom to be specified at equilibrium is given by phase rule as

$$F = C - P + 2 = (1 + 2) - P = 3 - P.$$

Three different possibilities arise depending on the number of phases existing and the number of degrees of freedom to be specified will be (i) $F = 2$ when $P = 1$ (bivariant system), (ii) $F = 1$ when $P = 2$ (univariant system) and (iii) $F = 0$ when $P = 3$ (invariant system). Thus for a one-component system the maximum number of degrees of freedom is two and hence such a system can be completely represented by a two-dimensional diagram. Temperature and pressure are the most convenient variables (degrees of freedom) to describe the equilibrium conditions of one-component systems. The important parts of such phase diagrams include (i) area (ii) boundary line or curve and (iii) point. Areas represent a bivariant system while lines and point represent the univariant and invariant systems respectively. These aspects are described with the help of phase diagrams for water and sulphur systems.

2.4.1 Water system

The phase diagram for the water system existing in three phases, namely, solid, liquid and vapour phases is shown in Figure 2.1.

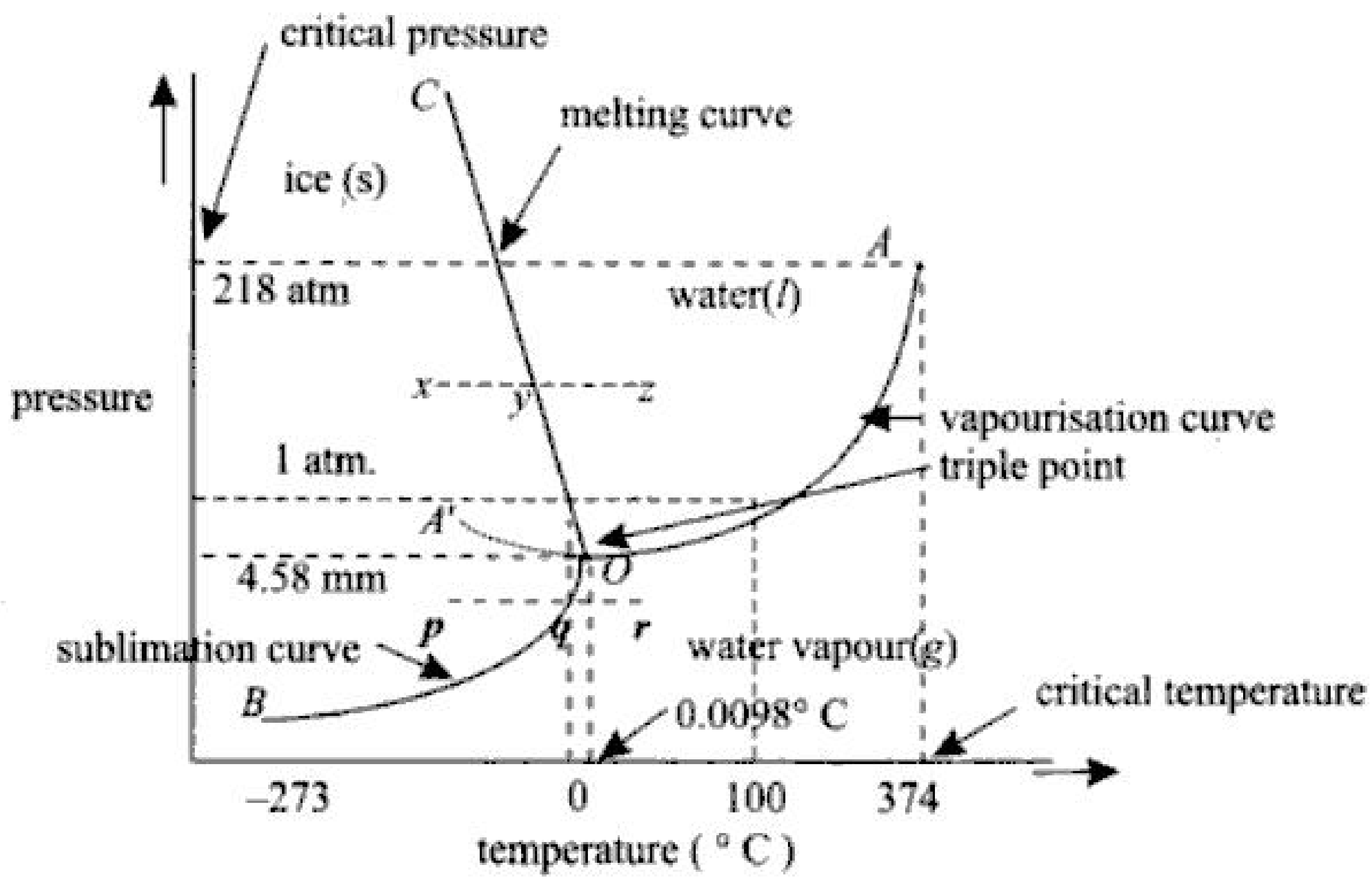


Fig. 2.1 Phase diagram of ice-water-water vapour system

There are three **areas** in the phase diagram as represented by *AOB*, *AOC* and *BOC*. Only one phase exists in each of these areas, namely, water vapour in *AOB*, liquid water in AOC and solid ice in *BOC*. In the area $F = 1 - 1 + 2 = 2$. It is necessary to specify both temperature and pressure coordinates to locate any point within these single-phase areas.

The **boundary lines** are *OA*, *OB* and *OC* representing the existence of two phases in equilibrium. The line *OA* is called the vapour pressure curve. Along the line *OA* liquid water and water vapour coexist and the phase rule requires that any one degree of freedom or variable is to be specified, to locate a point along the line. The degrees of freedom are given as $F = 1 - 2 + 2 = 1$. If the temperature is specified, the other variable namely, pressure automatically gets fixed. Thus at any specified temperature there is only one pressure at which water vapour is in equilibrium with liquid water. Similarly, at any specified pressure there is only one temperature at which the two phases coexist. The line *OA* has the upper limit at 374° C which is called the critical point. Above the critical temperature, the liquid phase merges with the vapour phase and the two phases cannot be distinguished from each other. Line *OB* is the sublimation curve of ice and represents the coexistence of water vapour and solid ice. The point B at –273° C represents the merging of the two phases. The line *OC* is the melting curve of ice and represents the coexistence of solid ice and liquid water at equilibrium. The line slopes towards the pressure axis indicating that the melting temperature of ice decreases with increasing pressure.

The **triple point O** is the meeting point of the three curves *OA*, *OB* and *OC* where all the three phases—solid ice, liquid water and water vapour coexist. The experimentally determined triple point corresponds to a temperature of + 0.0098° C and a pressure of 4.58 mm of Hg and represents an invariant system since there is no degree of freedom, $F = 1 - 3 + 2 = 0$. Even a slight variation of temperature or pressure from the specified values will cause the disappearance of one of the phases.

The curve *OA'* represents the equilibrium between the supercooled liquid—a **metastable phase** and solid ice. Normally liquid water solidifies at 0° C at one atmospheric pressure. However, it is possible to supercool clean liquid water free from any dust to several degrees below 0° C. The curve *OA'* is thus the vapour pressure curve of the supercooled water and vapour pressure of supercooled water is higher than that of ice. The metastable phase changes to the thermodynamically stable phase of ice even from a slight disturbance or the introduction of a crystal of ice as seed.

The practical application of phase rule for water system can be understood by considering the phase changes that occur along the lines ***xyz*** and ***pqr***. At the point *x* the only phase that can exist is ice and with increasing temperature along the line ***xyz*** ice melts at the point *y* on the curve *OC*, and at the point *z* only liquid water can exist. Similarly at a lower pressure along the line ***pqr***, the point ***p*** represents the existence of only one phase namely, ice which with increasing temperature changes into the vapour phase directly (sublimation) at the point ***q*** on the curve *OB*, and at the point ***r*** only the vapour phase exists. The principle of sublimation is of importance in freeze drying of thermally labile (unstable) products such as food, biological and pharmaceutical products which may decompose if dehydration by evaporation or drying at higher temperatures at atmospheric pressure is adopted. Freeze drying involves reducing the water content in the product (dehydration) by freezing it to solid ice at a low pressure of about 1 mm of Hg and then subliming ice to vapour at the same pressure so that it escapes from the product. The principle of sublimation is also used in the case of dry ice (solid carbon dioxide) used as a refrigerant. Sublimation of a solid occurs if it is heated under conditions such that, the partial vapour pressure is less than the triple point pressure. For solid carbon dioxide the triple point pressure is 5.11 atm. and hence the solid can be sublimed at one atmospheric pressure with the temperature remaining constant at – 78.5° C. Similarly iodine with a critical triple point temperature of 114° C and pressure of 90 mm of Hg sublimes into vapour at ambient temperatures because the partial vapour pressure is less than 90 mm even though the atmospheric pressure is 760 mm. However, solid iodine can be melted into a liquid by heating in a closed vessel.

2.4.2 Sulphur system

Polymorphism (allotropism in the case of elements) refers to the phenomenon of a solid substance exhibiting more than one crystalline phase each with a distinct melting point and physical properties. Sulphur exists in two polymorphic forms, the rhombic (S_R) and the monoclinic (S_M) form. In addition sulphur also exists in the melt (liquid) and vapour phase. However, for a single component system the maximum number of phases that can coexist is only three and hence all the four phases (two solid, one liquid and one vapour phase) cannot coexist. The phase diagram of the sulphur system is shown in the Figure 2.2.

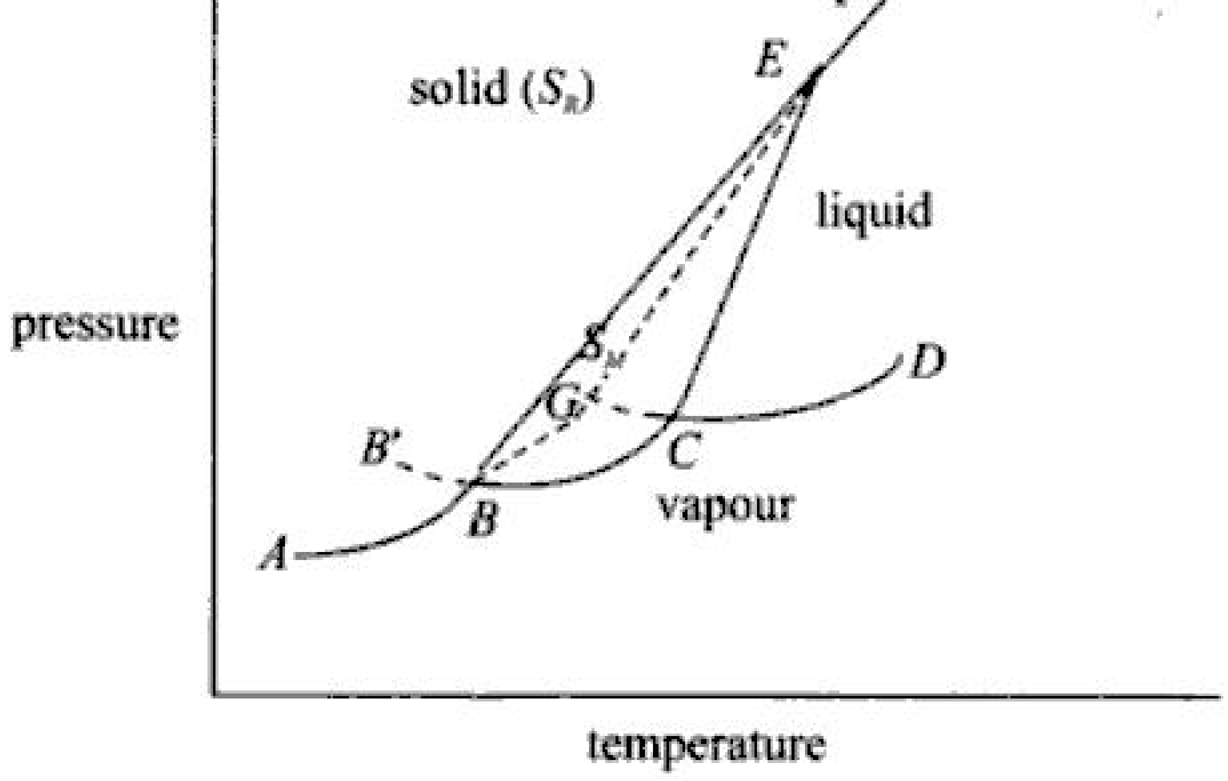


Fig. 2.2 Phase diagram of the sulphur system

The phase diagram shows four areas *ABCD*, *DCEF*, *ABEF* and *BCE*. The area below *ABCD* represents the region where only sulphur vapour exists. The region to the right of DCEF has only one phase namely, liquid sulphur. The area to the left of ABEF is the region where solid rhombic sulphur exists while the area enclosed within BCE solid monoclinic sulphur alone exists. The areas represent a bivariant system and hence both temperature and pressure must be specified to define the condition of any point within the given area.

The boundary lines *AB*, *BC*, *CD*, *BE*, *CE* and *EF* separating the various areas represent the univariant systems. The number of degrees of freedom to be specified is 1, either temperature or pressure is to be specified. ($F = 3 - 2 = 1$). There are four metastable curves shown in dotted lines *BG*, *CG*, *EG* and *BB'* in the Figure 2.2.

The line or curve *AB* extends between 50° C and 95.6° C and represents the vapour pressure curve of S_R. The vapour pressure is not measurable below 50° C and above 95.6° C S_R transforms into S_M. Thus the point *B* represents the *transition temperature* for S_R to S_M. Rhombic sulphur on rapid heating, melts to liquid sulphur at 115° C (point G) without going through the transition to S_M. The curve *BG* represents the metastable sublimation curve of rhombic sulphur.

The boundary line *BC* represents the vapour pressure curve of monoclinic sulphur and its melting at 120° C to give liquid sulphur. The curve *CD* is the vapour pressure curve of liquid sulphur while the curve *CG* represents the metastable vapour pressure curve of the supercooled liquid sulphur. The line *BE* is the transition of rhombic sulphur to the monoclinic sulphur. The line is sloping away from the pressure axis indicating that the transition temperature for the S_R to S_M increases with an increase in pressure. This is due to the fact that the denser phase of rhombic sulphur is relatively more stable compared to the lesser dense phase of monoclinic sulphur, as pressure increases. Since the formation of rhombic sulphur is accompanied by liberation of heat the transition temperature increases with increasing pressure. The line *CE* separates the monoclinic sulphur and the liquid sulphur and slopes to the right as density of the liquid phase is lesser. The line *EF* represents the melting of the rhombic sulphur to a liquid. The dotted line EG represents the metastable vapour pressure curve of the super cooledmonoclinic sulphur. The dotted line *BB'* represents the metastable vapour pressure curve of monoclinic sulphur.

The sullphur system also exhibits four triple points, *B*, *C*, *E* and *G*, the last one–*G* being a metastable one. At the triple point three phases coexist and hence the system is invariant with no degrees of freedom. If any of the conditions are changed one of phases will disappear. The phases at equilibrium at the triple points are as follows:

B – (95.6° C and 0.006 mm) – equilibrium of S_R, S_M and sulphur vapour
C – (120° C and 0.04 mm) – equilibrium of S_M, liquid sulphur and sulphur vapour
E – (151° C and 1288 atm) – equilibrium of S_R, S_M, and liquid sulphur

At the metastable triple point G (115° C and 0.03 mm) the three phases that coexist are rhombic sulphur, liquid sulpur and sulphur vapour.

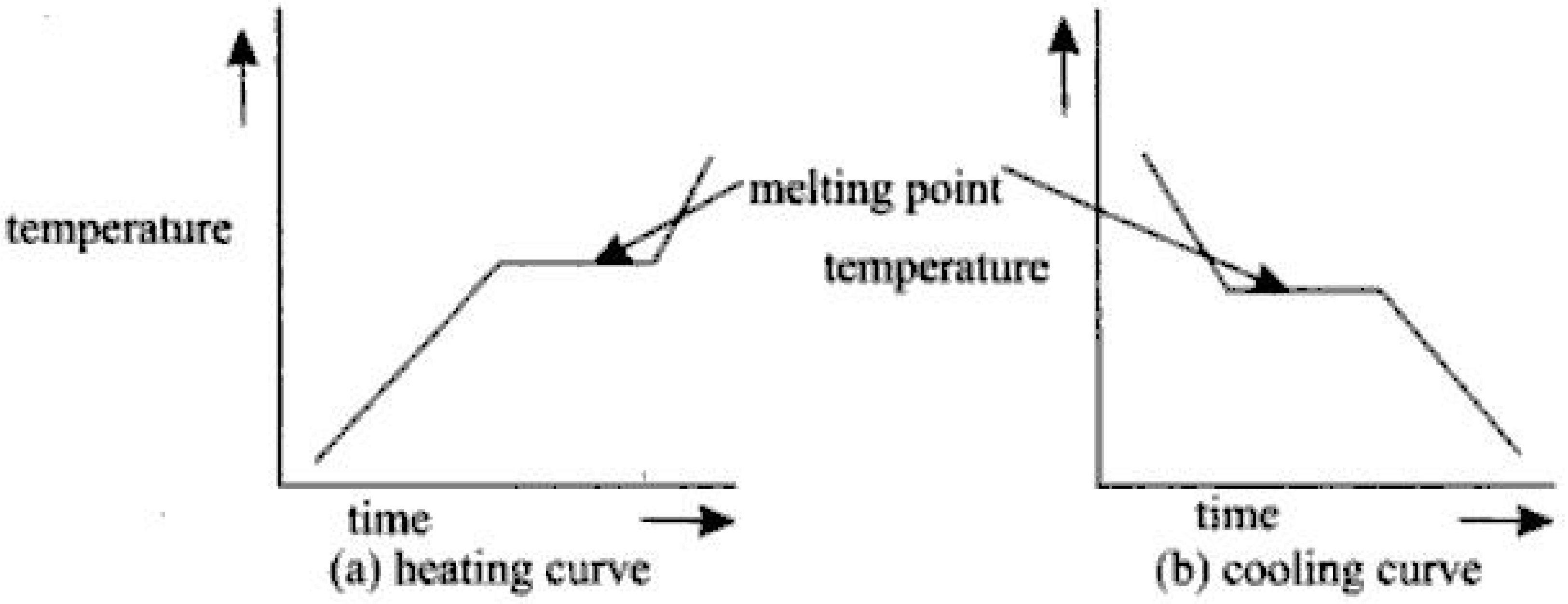
2.5 Phase Rule for Two Component Systems

According to the phase rule for a two component system the maximum number of phases that can exist will be four; $P = C - F + 2 = 2 - 0 + 2 = 4$. The degrees of freedom will be zero for a two component four phase system. The maximum number of degrees of freedom will be 3 if the two component system exists in a single phase; $F = C - P + 2 = 2 - 1 + 2 = 3$. The three degrees of freedom have to be temperature, pressure and composition. The phase diagram requires a three-dimensional representation.

However, in the case of solids such as alloys the vapour phase does not exist and hence the effect of pressure is negligibly small on the equilibrium. Experiments are carried out at atmospheric pressure (constant pressure) and the *condensed* or the *reduced phase rule equation* of $F = C - P + 1$ is sufficient to describe such *condensed systems* in which the vapour phase is not considered. The condensed phase rule thus relies only on two variables, namely, temperature and composition. The phase diagrams are called *temperature-composition diagrams*. These diagrams are obtained by thermal analysis.

2.5.1 Thermal analysis

The method involves the study of the heating curves, or more commonly the cooling curves (time-temperature relationships). The heating and cooling curve of a solid sample undergoing melting is shown in Figure 2.3.



(a) heating curve (b) cooling curve

Fig. 2.3 Heating and cooling curves of a solid undergoing melting

When a pure solid is heated slowly (~ 1° C/min) the temperature increases linearly with time until the solid starts melting. During the transition of the solid to the liquid phase the heat supplied is utilised to bring about the phase change (latent heat of fusion) and the temperature remains constant for a period of time till all of the solid is completely changed to liquid as indicated by the plateau in the heating curve. Once melting is completed the temperature increases again linearly with time. The temperature of the molten solid in its pure state on slow cooling (~1° C/min) decreases linearly with time till the freezing point is reached and the solid makes its appearance. The temperature remains constant over a period of time till all of the liquid is transformed into the solid phase giving rise to the plateau region in the cooling curve. After complete solidification the temperature decreases continuously with time. Similar heating and cooling curves are obtained for phase transitions between crystalline phases of a solid and the freezing of mixtures of solids of known composition.

2.6 Application of Phase Rule for Two Component Metal (Alloy) Systems

The behaviour of two component systems is of importance in engineering and may be studied conveniently under the following types, namely, (i) substitutional solid solutions, (ii) formation of a simple eutectic (iii) compound formation with a congruent melting point and with an incongruent melting point, (iv) partially miscible solids and (v) interstitial solid solutions.

2.7 Substitutional Solid Solutions

Substitutional solid solutions are obtained when one solid dissolves in another completely to form a homogeneous mixture. The solute atoms substitute for solvent atoms in the crystal lattice of the solvent. Substitutional solid solutions of unlimited solubility are formed by two elements having the same number of valence electrons, the same crystal structure and when their atomic radii of are almost the same or differ by less than 8%. Copper-nickel alloy system is an example of substitutional solid solution.

2.7.1 Copper-nickel alloy system

The phase diagram of copper-nickel system is shown in the Figure 2.4. The two elements are soluble in each other over the entire range of compositions. A homogeneous solid solution is a single phase and hence the system has a maximum of 2 phases, a solid and a liquid. The freezing points of pure copper and nickel are 1083° C and 1452° C respectively. The addition of nickel to copper raises the freezing point, while the addition of copper to nickel decreases the freezing point and hence the freezing point of a mixture of copper and nickel of any composition lies between the individual freezing points of the metals. The upper and the lower curves in the diagram represent the liquidus (freezing curve) and the solidus (melting curve) respectively. Only one phase namely, the liquid phase exists above the liquidus while the solid phase alone exists below the solidus curve. In between these two curves both solid and liquid phases coexist with both the components forming a continuous series of liquid and solid solutions in equilibrium, the composition being determined by tie lines.

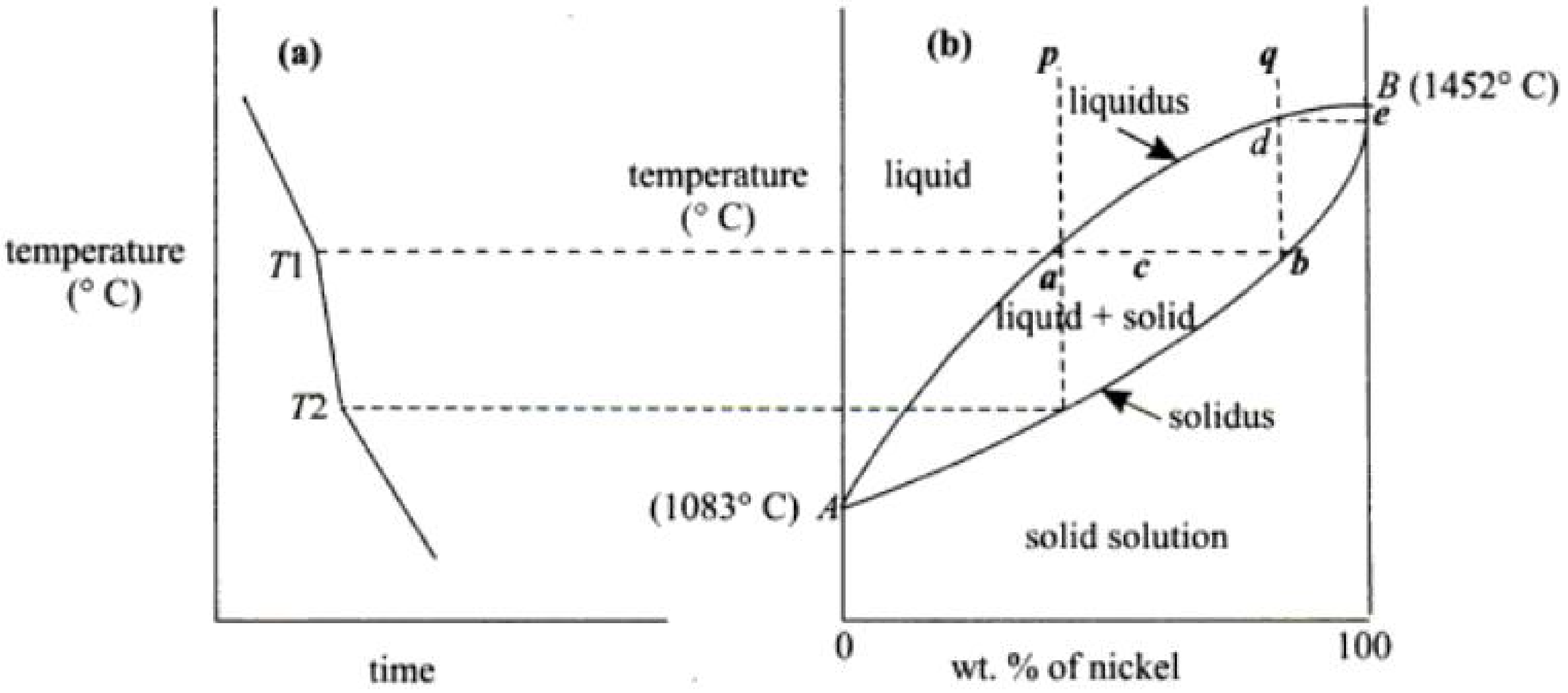


Fig. 2.4 (a) Cooling curve and (b) temperature-composition diagram of copper-nickel system

The number of phases at the point ***p*** is one (liquid phase) and hence for two component single phase system, the number of degrees of freedom is 2. Both temperature and composition have to be specified to describe the point. Cooling the liquid at point ***p*** to temperature *T*1 results in the separation of the solid and the system becomes a two phase system with one degree of freedom. The compositions of the liquid phase and the solid phase at a temperature of *T*1 are given by points ***a*** and ***b*** respectively. Further cooling changes the composition also. The solid formed is neither pure copper nor pure nickel but a solid solution of nickel in copper. At point ***c*** the system consists of a liquid of composition given by point ***a*** on the liquidus curve in equilibrium with the solid solution whose composition is given by the point ***b***. The dotted line ***acb*** is called the tie line. The relative proportions of the two phases at the point ***c*** is given by lever rule, according to which

$$\frac{\text{Amount of Solid}}{\text{Amount of Liquid}} = \frac{ac}{bc}$$

The solid of composition *b* that separates out may be melted separately to a give a liquid of composition ***q*** which on cooling to a temperature corresponding to *d* gives out a solid solution of composition ***e***. It can be seen that the solid solution of composition ***e*** is richer in nickel compared to that of the solid solution of composition ***b***. The procedure may be repeated to get ultimately pure nickel. This process of separation of a mixture into its pure components is called *fractional crystallization* and forms the basis of *zone melting* or *zone refining*

2.7.2 Zone refining

Zone refining is used extensively for the preparation of highly pure metals required for the electronic industries and actually involves carrying out fractional crystallisation repeatedly. *A* furnace is passed from one end (A in the Figure 2.5) to the other end (B) of a long uniform bar of the solid to be purified at a slow rate in the range of 3-4 cm/hour. The furnace on reaching the end *B* is quickly brought to the end *A* for the second pass of the furnace. The passage of the furnace from *A* to *B* is repeated several times. *A* liquid zone is formed as the solid melts and the moving liquid zone melts the solid in front of it. Solid crystallises out behind the moving zone. The impurity distributes itself between the solid and liquid phases such that the ratio of the concentrations of the impurity in the two phases is a constant *K* at a given temperature. The constant is called the *segregation constant* or *partition constant*. The value of $K < 1$ for impurities which depress the freezing point and $K > 1$ one for those which increase the freezing point.

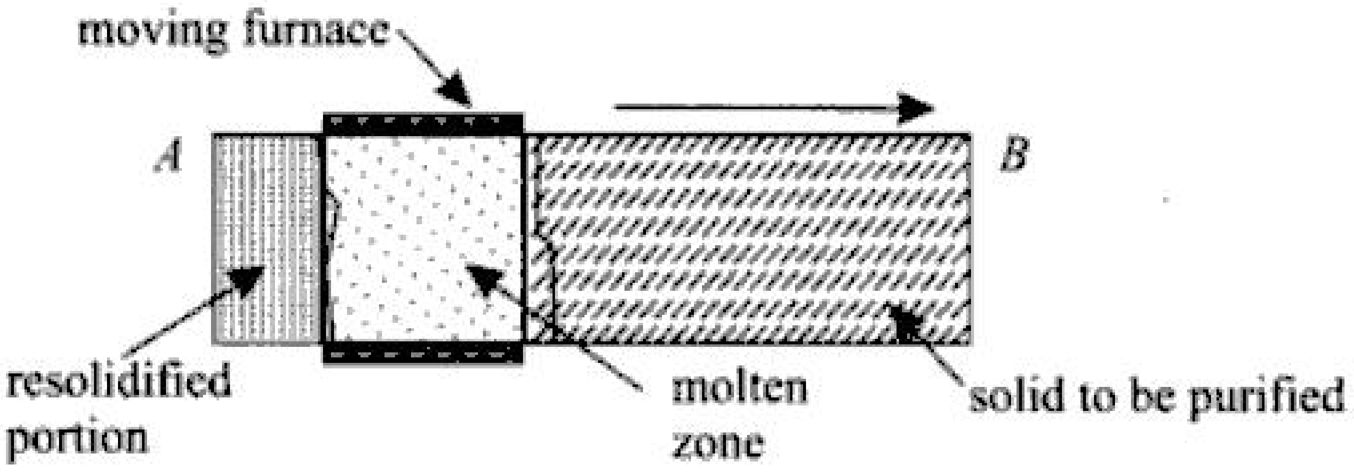


Fig. 2.5 Representation of zone refining

If $K < 1$ the liquid contains more impurity, while the solid crystallising out of the liquid has lesser impurity. The passage of the zone along the bar leads to an increase in the concentration of the impurity in the liquid and since K is a constant the concentration of the impurity in the solid crystallising out also increases proportionately. The moving zone thus sweeps all the impurities along the bar towards the end B. It has been shown that for *K* values in the range 0.1-0.5 about 20 zone passes will produce an extremely pure metal at the end A.

The segregation constant $K > 1$ for impurities which elevate the freezing point. In such cases the impurities tend to remain in the solid phase and with multiple passes of the furnace the impurity accumulates at the end A.

2.8 Eutectic Forming Systems

When two metals are completely miscible in the liquid state but do not have any solid-solid solubility, the phase diagram consists of two solubility curves intersecting at a point called the *eutectic point* which is characterised by the temperature called *eutectic temperature* and a composition called *eutectic composition*. Eutectic (Gk = easily melting) point has a unique composition in that it has the lowest melting point. Eutectic temperature is the lowest or minimum temperature at which the liquid phase can exist. Two component alloys such as bismuth-cadmium, lead-silver, copper-silver, zinc-cadmium and zinc-aluminum are examples of eutectic forming systems.

2.8.1 Bismuth-cadmium system

Condensed phase rule will be applicable to the alloy system as the gaseous phase is practically absent. Pure bismuth melts at 271° C and pure cadmium melts at 321° C. The two metals are completely miscible in the liquid phase. Addition of cadmium to pure liquid bismuth lowers the freezing point below 271° C and similarly addition of bismuth to liquid cadmium lowers the freezing point below 321° C. The cooling curves for a few compositions (dark lines) and the phase diagram are shown in Figure 2.6.

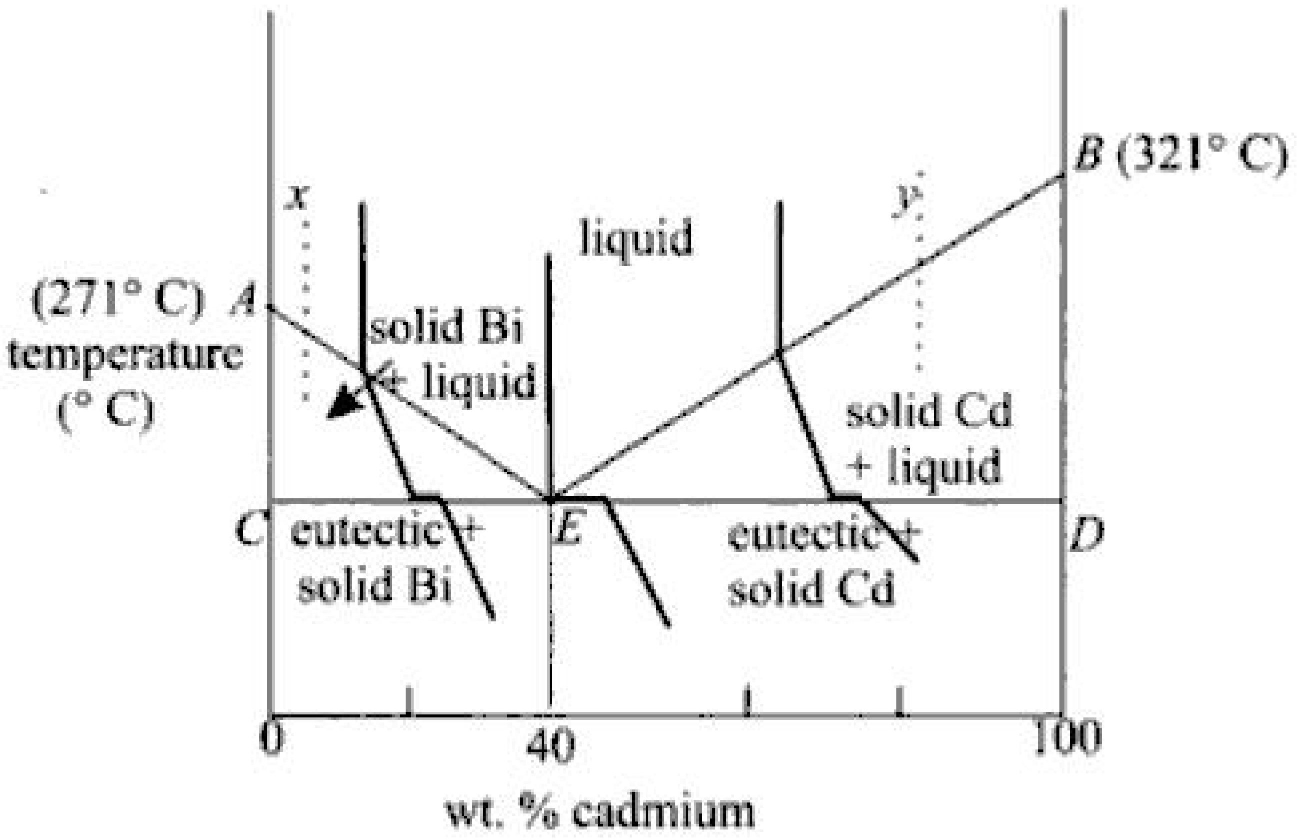


Fig. 2.6 Phase diagram of bismuth-cadmium system

The line AE represents the freezing point curve of bismuth as cadmium is added to pure bismuth. The freezing point decreases continuously with added cadmium till the lowest freezing temperature (144° C) at E is reached for 40% cadmium – 60% bismuth mixture. Further addition of cadmium results in its separation as solid phase, as it does not go into solution. Along the line AE the system is univariant with one degree of freedom ($F = 3 - P = 3 - 2 = 1$). The line BE represents the freezing point curve of cadmium and the effect of the addition of bismuth to cadmium. The freezing point gradually decreases till it reaches the lowest temperature at E. The line BE is also univariant just as the line AE.

The two lines AE and BE meet at E which is the eutectic point where the three phases namely, solid bismuth, solid cadmium and their solution, coexist and the system is invariant with no degrees of freedom ($F = 3 - P = 3 - 3 = 0$). It represents a fixed temperature of 144° C (eutectic temperature) and a fixed composition of 40% Cd + 60% Bi (eutectic composition). No mixture of bismuth and cadmium has a melting point lower than this composition.

The eutectic mixture has certain characteristic features. The mixture with an eutectic composition shows a sharp melting point just like a compound. However the eutectic mixture is not a compound as the two components are not present in a molecular ratio. When one of the components is added to the eutectic mixture the mixture melts at a higher temperature (in contrast such an addition to a compound will either decrease the melting point or does not alter it). The physical properties of the mixture (e.g., density) are equal to the mean values of the two components.

The area above the curve *AEB* includes the liquid phase containing the completely miscible bismuth and cadmium. Cooling the liquid of composition *x* down the dotted line is possible till the temperature reaches the intersection point of the dotted line with the line *AE*. At this temperature solid bismuth crystallises out. Further cooling brings out further crystallisation of bismuth and the liquid becomes richer in cadmium and the freezing point of the liquid decreases till it reaches the eutectic temperature. Cooling the liquid of a composition *y* down the dotted line is feasible till the temperature reaches the intersecting point between the dotted line and line *BE*. At this point cadmium crystallises out and the remaining liquid becomes richer in bismuth with its freezing point moving down towards the eutectic temperature.

2.8.2 Lead-silver system

The two component lead-silver system is similar to the bismuth-cadmium system in that, the metals are miscible in the liquid state, while in the solid state they form an eutectic mixture of a composition 2.6% Ag + 97.4% Pb melting at 303° C. The phase diagram (Figure 2.7) shows the freezing point curves *AE* for silver and BE for lead meeting at the eutectic point E. The descriptions of the lines, areas and the invariant eutectic point are similar to the description given for the bismuth-cadmium system.

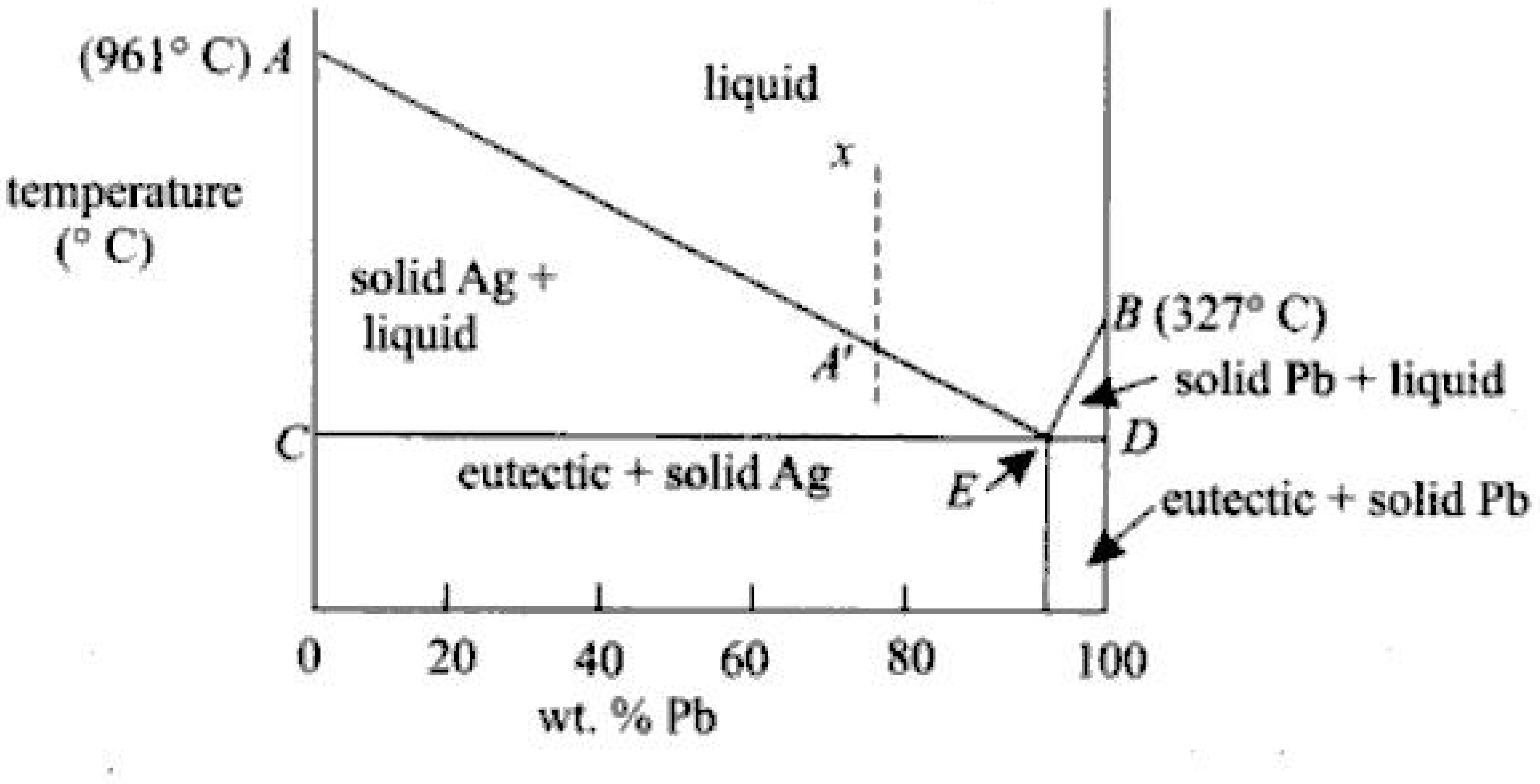


Fig. 2.7 Phase diagram of lead-silver system

The phase diagram is useful in the recovery of pure metals from alloys of different compositions by fractional crystallisation. This is of practical significance in the Pattinson's process of desilverization of lead. If the melt of a sample of argentiferous lead containing more than 2.6% of silver is allowed to cool from point *x* along the dotted line, pure silver will crystallise out along line *A'E* till the remaining liquid reaches the eutectic composition containing 2.6% Ag. Similarly if the melt contains less than 2.6% Ag, pure lead will separate out, leaving the liquid richer in silver, along the line BE till the eutectic composition is reached.

2.9 Systems Involving Compound Formation

The two components *A* and *B* may interact to form a compound with a definite stoichiometric composition and a sharp melting point. If the composition of the compound remains the same in the solid and the liquid states the compound is said to have a *congruent melting point*. In some systems compounds are formed but the compounds are not stable till their melting point. When such compounds are heated instead of melting congruently they decompose to yield a new solid phase and a solution of composition different from that of the solid phases. The compound is said to undergo a *transition* called *peritectic reaction* or *incongruent fusion*.

2.9.1 Compound formation with congruent melting

The phase diagram of such a system shows two eutectic points separated by a hump as shown for a zinc-magnesium alloy system (Figure 2.8). The composition corresponding to the hump is useful in deducing the formula of the compound and the maximum point of the hump indicates the melting point of the compound. The compound formed in the zinc-magnesium system is $MgZn_2$ with a congruent melting temperature of 590° C.

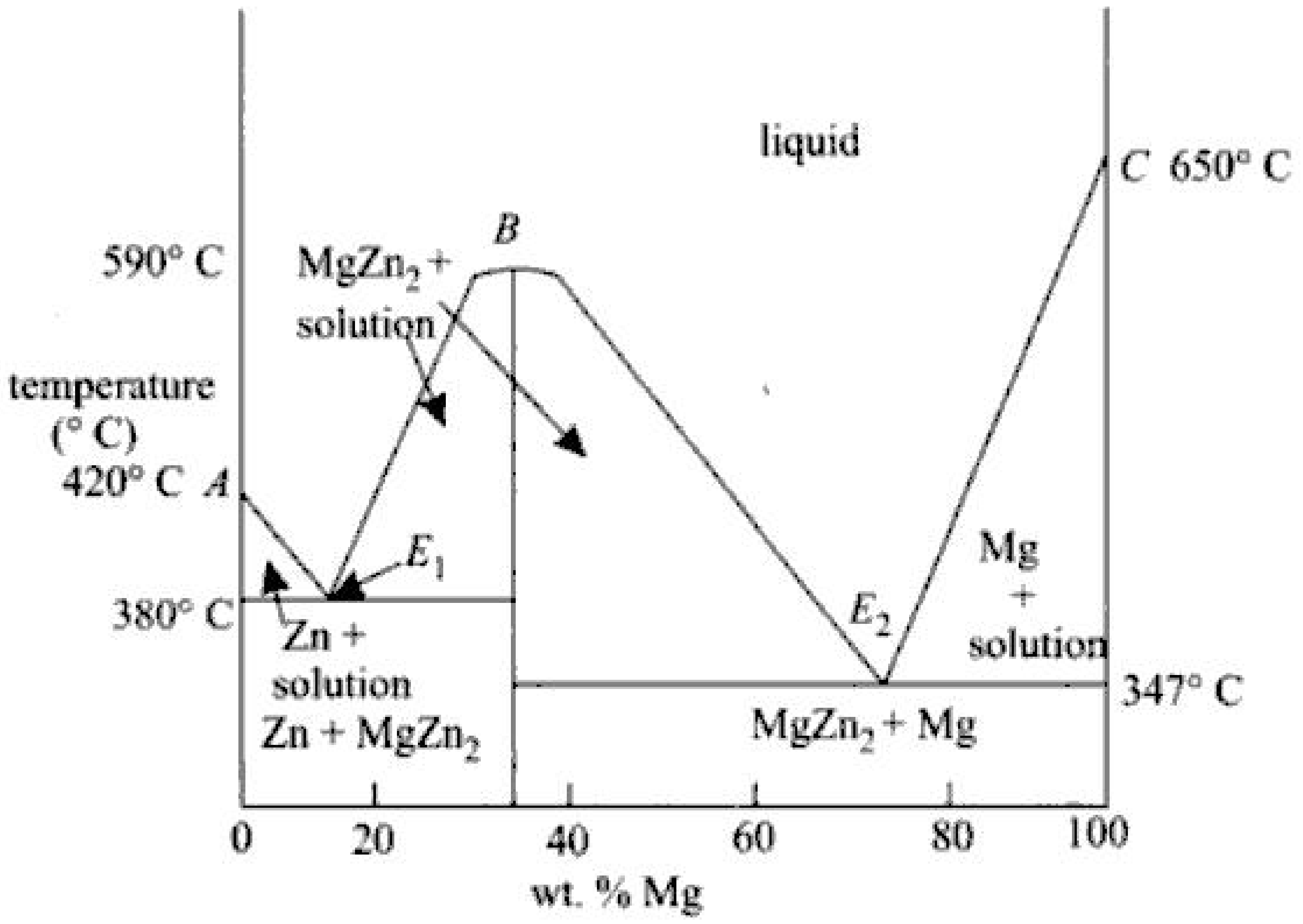


Fig. 2.8 Phase diagram of a Mg-Zn alloy system

The metals zinc and magnesium melt at 419.5° C and 650° C respectively. The phase diagram may be considered as a combination of two phase diagrams of simple eutectic forming systems (e.g. Bi-Cd or Pb-Ag system) placed side by side. The part of the phase diagram on the left side consists of the two components Zn and $MgZn_2$ while that on the right consists of the two components $MgZn_2$ and Mg. The line AE_1 represents the boundary between the liquid and solid zinc and similarly the line CE_2 represents the equilibrium between the liquid and solid magnesium. The two eutectic points E_1 and E_2 have compositions of Zn (71%) + $MgZn_2$ (21%) melting at 380° C and $MgZn_2$ (61%) + Mg (39%) melting at 347° C respectively representing the invariant systems. The curve E_1BE_2 encloses a region in which the liquid and solid $MgZn_2$ coexist. The maximum point *B* of the hump E_1BE_2 corresponds to a composition of $MgZn_2$ (Mg (33.33%) + Zn (66.7%)) with a congruent melting point at 590° C. The sharpness of the maximum is indicative of the stability of the compound while a flat maximum as shown in the present case is indicative of appreciable dissociation of the compound.

2.9.2 Compound formation with incongruent melting

The phase diagram of the gold-antimony system forming a compound AB_2 ($AuSb_2$) with an incongruent melting point is shown in Fig. 2.9. The point *D* represents the hypothetical melting point of the compound called peritectic point (Gk. = melting around). The compound on melting decomposes and yields pure *B* as the new solid phase and a liquid whose composition is different from that the pure solid *B* or the solid compound AB_2. The solid in the region to the right of the dotted line *DD′* consists of two phases, a core of *B* surrounded by a coating of AB_2. The point E represents eutectic point.

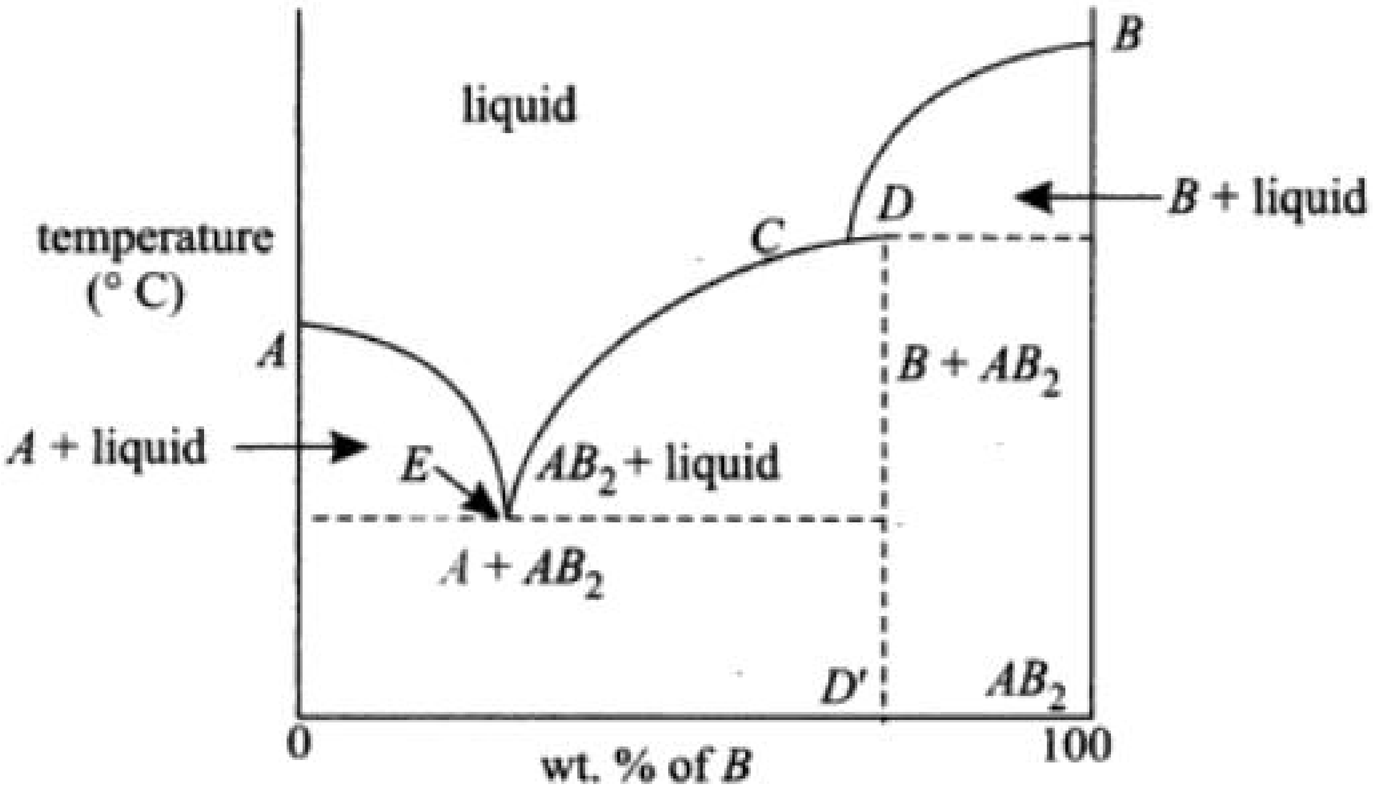


Fig. 2.9 Phase diagram of a system forming a compound with incongruent melting (e.g. Au-Sb system)

2.10 Partially Miscible Solids

Examples of partially miscible solids include the lead-tin system and the copper-aluminum system.

2.10.1 Lead-tin system

Lead is soluble in tin only up to 2.6% while tin is soluble in lead to the extent of 19.5% forming solid solutions. The phase diagram of the lead-tin system is shown in Figure 2.10. Lead melts at 327° C while tin melts at 232° C. The lead-rich solid solution is called *α*- phase and lies to the left-end of the diagram (to the left of the curve *ADF*. The phase is a saturated solution of tin in lead. The tin-rich phase called the *β*-phase lies at the right end of the diagram (to the right of the curve BCG) and is a saturated solution of lead in tin. A miscibility gap exists corresponding to the coexistence of *α*- and *β*- phases in equilibrium.

Three phases *α*-, *β*- and the liquid can coexist and the system based on condensed phase rule becomes invariant. The phase diagram exhibits a discontinuity which may be either a eutectic point or a transition point. Eutectic point is shown by the lead-tin system. The curves *AE* and *BE* are the liquidus curves while the *ADE* and *BCE* are the solidus curves. The points *D* and *C* represent the maximum solubility of tin in lead and lead in tin respectively. The solubility decreases with the decrease in temperature. At the eutectic point E the solid phases in equilibrium are the conjugate solid solutions and not the pure components. The curves *DF* and *CG* represent the variation of the composition of the conjugate solid solutions as a function of temperature. The eutectic mixture melts at 182° C and contains 60% lead.

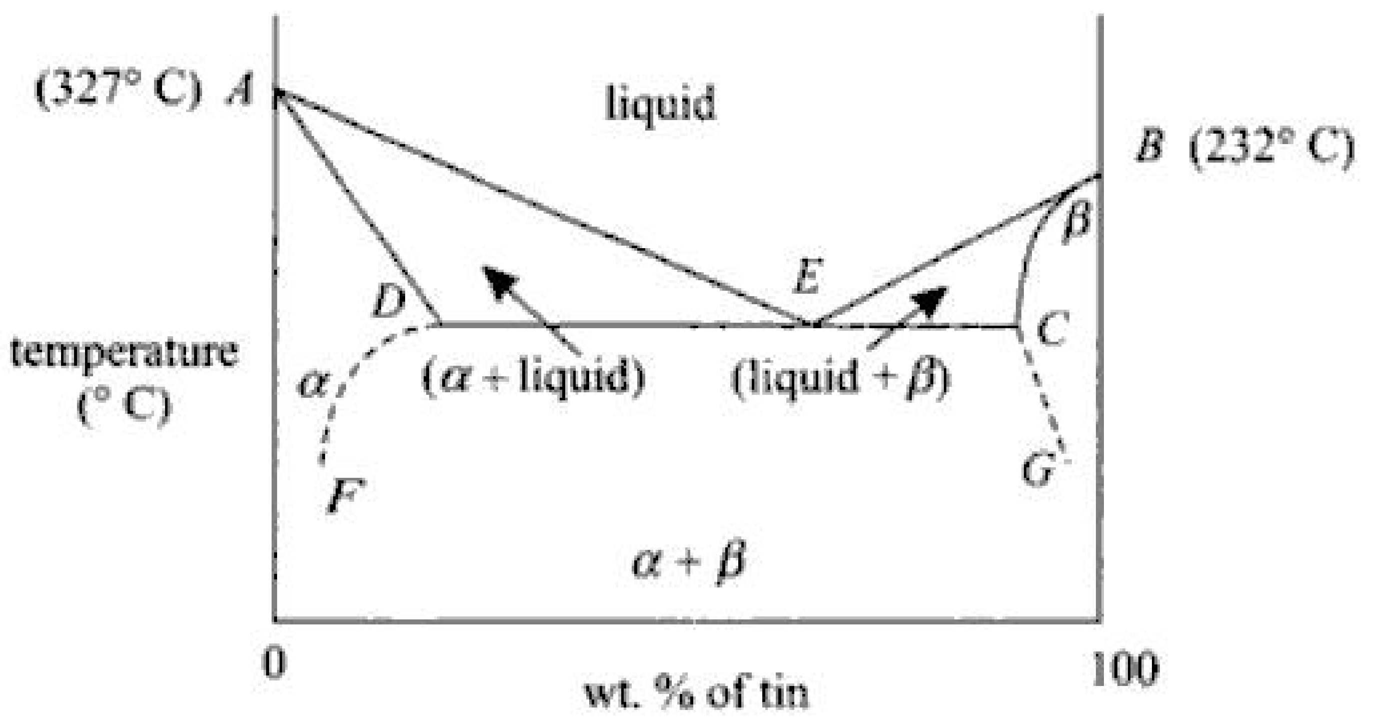


Fig. 2.10 Phase diagram of lead-tin system

Lead-tin alloys are fusible and are used as solders for metal-joining processes. The eutectic alloy of 60% lead-40% tin is used for soldering of electrical connections which require a metal-metal bonding with minimum heating. The more common plumber's solder has a composition of 50% lead- 50% tin melts rapidly, flows freely and with a wider range of freezing allows the wiping of the joint while the alloy is still in a pasty condition. It also provides a bright surface finish after soldering. Printing industry uses type metal, a ternary alloy of lead, antimony and tin. The addition of antimony to the lead-tin alloy hardens it and also makes the alloy expand on solidification.

2.10.2 Copper-aluminum system

The two metals are partially miscible in the solid state. The phase diagram is shown in Figure 2.11.

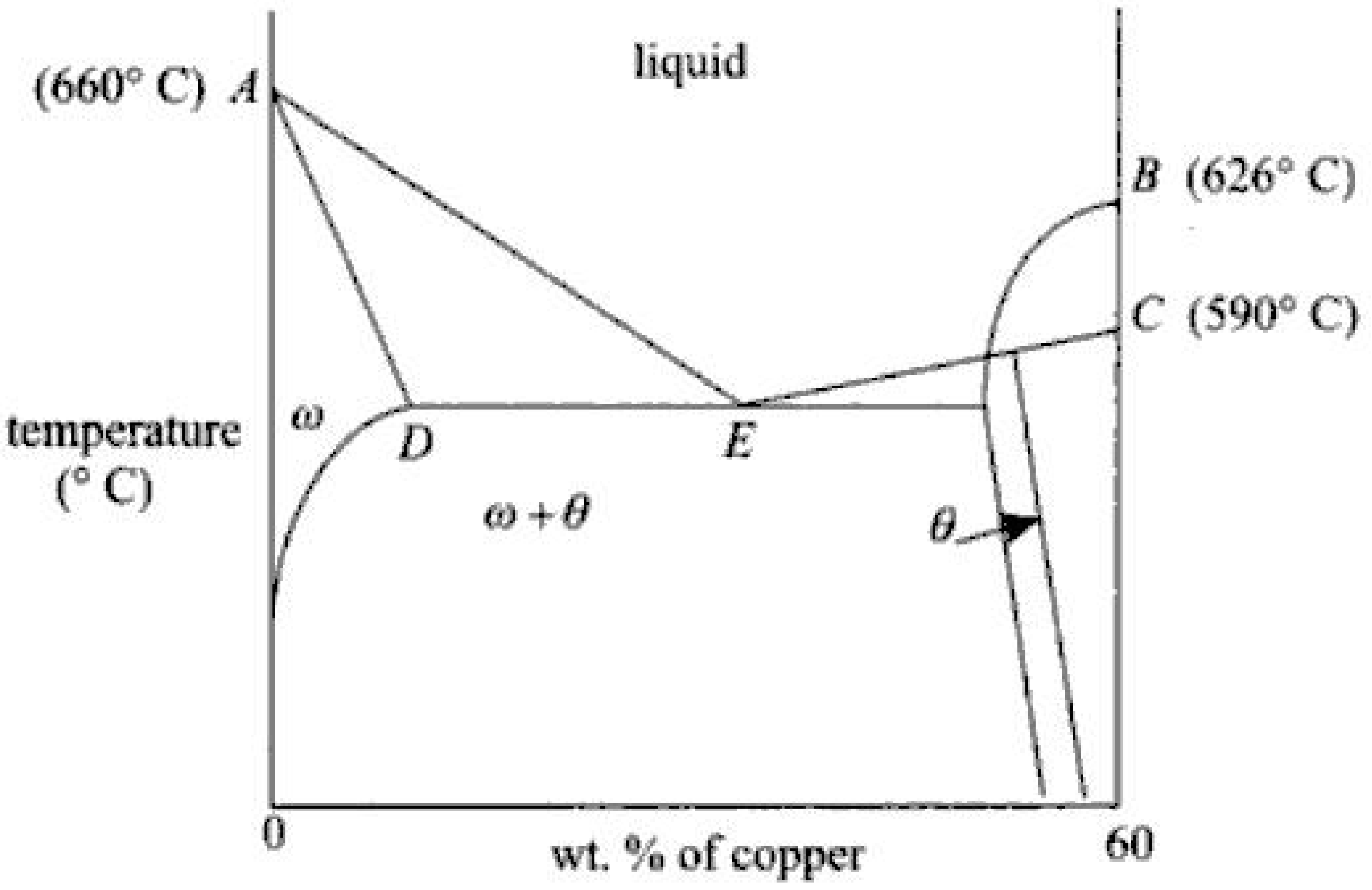


Fig. 2.11 Phase diagram of copper-aluminum system

The solid solution ω is formed at lower concentrations of copper in aluminum, the point D corresponding to 5.7% of copper. The point *E* at 548° C represents the eutectic between the solid solution ω and another intermediate solid solution θ. The eutectic solid contains 5.7% of copper while the eutectic liquid has a composition of 33% copper.

Copper-aluminum alloy containing 8% copper and the rest aluminum contains a mixture of ω phase and the eutectic $\omega + \theta$ solid solution. The alloy finds extensive use as a casting alloy in aluminum foundries. The alloy also with small amounts of silicon, iron and zinc has good mechanical properties and is used in automobile industry for crank cases, transmission housings, in washing machines and vacuum cleaners.

2.11 Interstitial Solid Solutions: Iron-Carbon System

Interstitial solid solutions are formed when the alloying elements differ widely in their atomic sizes and are best represented by the iron-carbon system. Pure iron is not useful for fabrication of structural components because of its weak mechanical properties. Carbon, though a non-metallic element forms alloys with iron to give various types of steel and improves the mechanical properties of the base metal to a large extent. The size of carbon atoms is small compared to that of iron atoms and hence occupies interstitial positions in the lattice formed by the iron atoms. The miscibility or solubility of carbon in iron depends on the crystal structure of iron, which in turn depends on the temperature, as pure iron exists in three allotropic modifications of α, γ and δ forms.

The cooling curve of pure molten iron shows the allotropic transformations as shown in Figure 2.12.

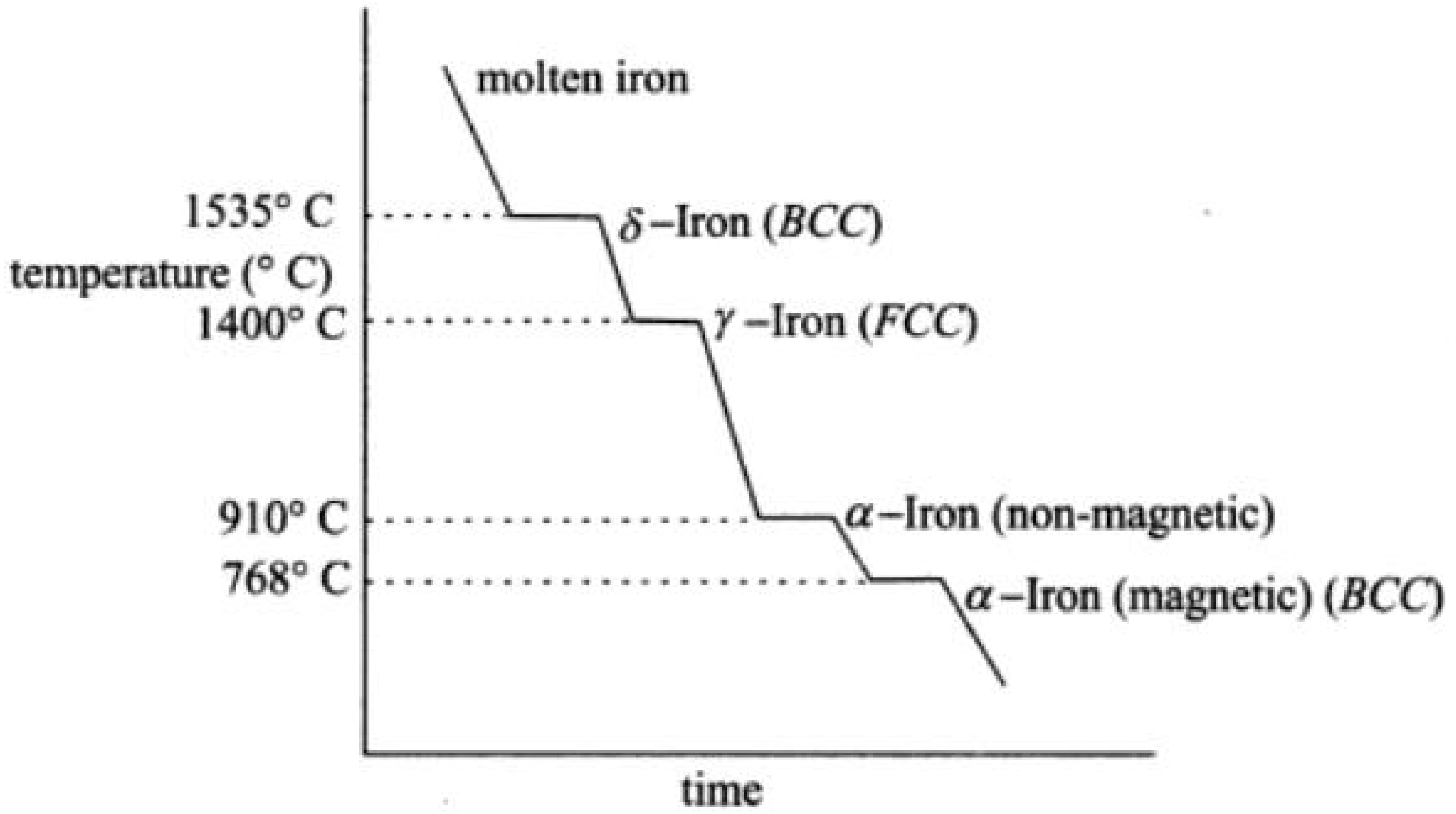


Fig. 2.12 Cooling curve of iron showing allotropic transformations

The low temperature allotropic form called the *α-iron* has a body-centered cubic (*BCC*) structure which is stable up to 910° C. The metal is soft and ductile and shows ferromagnetic properties below the Curie temperature of 768° C. In the temperature range between 910° C and 1400° C, *γ-iron* with a bigger face-centered cubic (*FCC*) structure is stable. This allotropic form is also soft and ductile. The high temperature allotropic form *δ-iron* has a *BCC* structure and is stable beyond 1400° C till it melts at 1535° C. None of the allotropic forms of pure iron are as useful as their alloys with carbon.

The solubility of carbon in *BCC* α-iron is quite low (~ 0.3% w/w) due to the small size of the interstitial sites which cannot accommodate even small atoms such as carbon. When the carbon content increases beyond 0.1%, α-iron changes over to γ- iron. The γ- iron can dissolve carbon to an increased extent of 1.7% w/w. The interstitial solid solution of carbon in γ- iron is called *austenite* steel. The transition temperatures of iron are influenced by the alloying elements, particularly carbon. For example the transition temperature of pure α-iron to γ- iron occurs at 910° C but with 0.3% carbon the transition commences even at 700° C and is completed at 800° C. With higher carbon content the whole transition is completed at around 700° C.

Pig iron as obtained from the blast furnace contains more than 4.3% carbon. The carbon is burnt off to give wrought iron containing less than 0.02% carbon. Wrought iron is extremely tough and ductile. It can be easily welded and forged. Cast iron is also an alloy containing carbon > 1.7% (up to 6.67%) and the excess carbon existing as graphite or as iron carbide. Steel is manufactured in the open hearth or Bessemer process by burning away the excess carbon and bringing down its percentage below 1.7%. Iron alloys containing carbon in the per cent range of 0.03-1.7 are called mild steels. Steel is an inhomogeneous mixture of *ferrite* and *cementite*. The mass is known as *pearlite* because of its peculiar layer structure consisting of alternate layers of ferrite and cementite. Ferrite is a solid solution of carbon in α-iron with a maximum carbon content of 0.035% at 723° C and 0.007% at room temperature. Ferrite is often considered to be pure α-iron. Cementite is iron carbide with a specific composition of Fe_3C (not a molecular compound) and a complex orthorhombic structure.

A steel of purely pearlite structure (0.8% carbon) is too hard to be of any structural use. The structure of steel containing 0.2–0.3% carbon is about one-third cementite and two-thirds ferrite while with 0.6% carbon the steel is composed of two-thirds cementite and one-third ferrite. More of ferrite makes pearlite soft and more of cementite makes it hard. The desired qualities of steel such as softness or hardness and toughness or brittleness for specific uses depend on the fineness or coarseness of the structure of ferrite and cementite. The structure and the grain size are controlled by quenching and/or annealing at critical ranges of temperature and the operation is generally called heat treatment of steel.

The formation of different phases in the iron-carbon system is conveniently explained with a phase diagram (temperature-composition diagram) shown in Figure 2.13 It can be seen that the composition is restricted to 6.67% of carbon and the phase diagram is actually that of γ-iron-iron carbide (F_3C) system. The iron carbide decomposes at higher concentrations of carbon. When carbon is dissolved in pure molten iron, the freezing point (1535° C) decreases as δ-iron is formed. As the carbon concentration increases beyond 0.5% the δ-phase disappears and the freezing point continues to decrease till 1130° C, the eutectic temperature at which the carbon content is 4.3%. The iron-carbon alloy containing 4.3% carbon solidifies instantaneously at the eutectic temperature into a mixture of austenite and cementite called *ledeburite*. Ledeburite is the major phase of pig iron and contributes to the hard and brittle nature of pig iron. At temperatures lower than 723° C ledeburite transforms into pearlite and cementite. Molten alloys containing less than 4.3% carbon solidify gradually on cooling passing through a pasty consistency. Addition of carbon beyond 4.3% till 6.67% increases the freezing point along the curve *EB* and beyond the carbon content of 6.67% cementite decomposes.

The transformation of pure γ-iron (1400–910° C) with an increasing carbon content is shown in Figure 2.13. The curve *DF* represents the decrease in the freezing point of γ-iron below 910° C as more carbon dissolves in the bigger FCC structure. The point F is the second eutectic point in the iron-carbon phase diagram at 723° C and carbon content of 0.83%. The eutectic occurs in a completely solid region and hence, it is called a eutectoid (eutectic like). Pure iron changes from the γ to α form only at 910° C but this transition is shifted to a lower temperature of 723° C when iron is alloyed with 0.83% carbon. At this eutectoid temperature the austenite phase decomposes instantaneously into the pearlite phase.

The formation of austenite or pearlite can be understood from the phase diagram. For example on cooling a sample of hypoeutectoid steel containing less 0.8% carbon, along the line *xx* in the phase diagram, solid austenite separates at point ***a*** on the curve *AE*. The separation of austenite is completed at point ***b*** on the curve *AC*. Further cooling results in the separation of ferrite at point *c* on the curve *DF*. The composition of separated ferrite varies along the curve *DG* while that of the remaining austenite varies along *DF*. As the temperature decreases to the eutectoid temperature of 723° C precipitation of the eutectoid mixture (pearlilte) of ferrite and cementite from austenite occurs.

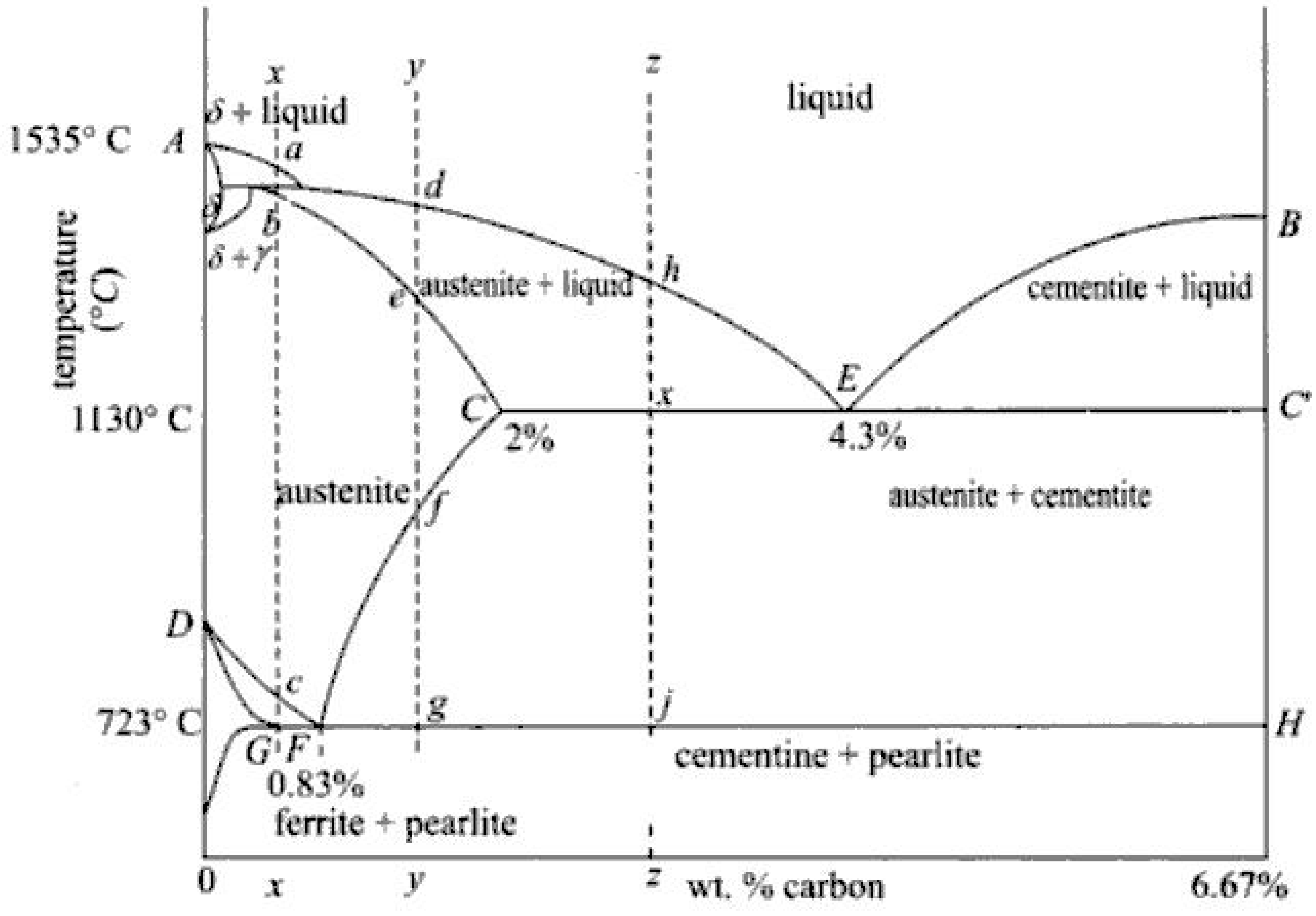


Fig. 2.13 Phase diagram of iron-carbon system

Pearlite is the only phase obtained when steel with 0.8% carbon is cooled from higher temperatures to 723° C. Steel with carbon content greater than 0.8% (hypereutectoid steel) is cooled along *yy*, austenite separates out at the point *d* on the curve *AE* and the process is completed at point *e* on the curve *AC*. Further cooling results in the separation of cementite at a point *f* on the curve *FC*. Once the temperature reaches 723° C pearlite formation occurs at the point *g* on the line *FH*. At lower temperatures a mixture of pearlite and cementite exist.

Cast iron containing less than 4.3% carbon on cooling undergoes transformations along the line *zz* represented by points *h* along the curve *AE*, *i* along *CE* and *j* along FH. Austenite begins to separate at point *h* and at point *i* (1130° C) the eutectic mixture of ledeburite (austenite and cementite) separates out. The eutectic mixture on cooling transforms gradually into cementite with the composition varying along CF till the point *j* where the remaining austentite changes into pearlite.

The phases formed in the iron-carbon system under equilibrium conditions only are shown in the phase diagram. Equilibrium conditions are established only when the cooling rates are very slow. When steel is quenched, that is cooled rapidly, austenite undergoes diffusionless transformation to a metastable phase called *martensite* (named after the German metallurgist Martens). Martensite is a supersaturated interstitial solid solution of carbon in α-ferrite with a distorted *BCC* or tetragonal structure. Microscopic examination of martensite reveals a series of fine needle like structures. Martensite is extremely hard and strong, the hardness being attributed to the efficient filling up of the void space in the BCC structure with carbon atoms which prevent slippage between planes of iron atoms. Another metastable phase called *bainite* (named after the American metallurgist Bain) is formed when steel is quenched to temperatures between 535° C and 260° C and allowed to undergo isothermal transformation. Bainite consists of a mixture of ferrite and cementite with fine needle like structures.

2.11.1 Heat treatment of steel

Heat treatment involves the combination of heating and cooling of a metal or alloy in one or more temperature cycles to confer desirable physical properties to the metal or alloy. Heat treatment of steel may be carried out under near equilibrium conditions to improve the ductility or under non-equilibrium conditions to enhance the hardness. During heat treatment the size and shape of the grains or the composition of the phase undergoes changes with respect to the microconstituents. In addition any internal stresses present are relived.

Plain carbon steel on heating to a temperature > 723° C and maintained at this temperature for a sufficiently long time allows the formation of the austenite phase and the dissolution of more carbon in the *FCC* structure. On slow cooling of the austenite phase transformation of *FCC* to *BCC* occurs and the excess carbon forms cementite. If the steel is *quenched* by plunging into water or oil to 204° C or a lower temperature the carbon atoms do not have sufficient time to form cementite but remain trapped in the *BCC* lattice. The excess carbon precipitates out in the hot metal and prevents the slipping of the planes. Thus quenched steel is quite hard and strong but has lower ductility. This heat treatment is called *transformation hardening*. Hardening involves the transformation of austenite to martensite or the bainite phase, making the steel hard. The quenched steed is not useful for construction purposes because of its brittleness. Therefore quenching is always followed by another heat treatment process called *tempering*. The quenched steel is tempered by reheating to below the α-iron- to-γ- iron transition temperature. The residual stresses and strains are relieved and the excess of carbon is rejected in the form of ε-carbide ($Fe_{2.4}C$). By tempering the steel becomes tougher and ductile. Tempering is carried out at about 200° C to make hard steel resistant to abrasion or at higher temperature (~540° C) to make tough steel capable of withstanding shock loads.

Annealing involves heating and holding the steel at a suitable temperature for some time to facilitate the dissolution of carbon in γ- iron followed by a slow cooling in a controlled manner in a furnace. Steel is softened and becomes ductile and machineable. However annealing decreases the hardness and strength of steel. Annealed hypereutectoid steels contain cementite. They are not soft but can be machined easily. In contrast annealed hypoeutectoid steels contain ferrite and are relatively soft and malleable.

Normalizing is yet another heat treatment involving the cooling of the hot steel more rapidly as compared to annealing but less rapidly when compared to quenching, usually carried out to convert a soft and ductile steel into a strong and ductile sample. The homogeneous structure of steel is recovered with refinement of grains and removal of internal stresses. Toughness increases and the normalized steel is amenable for use in engineering works.

Case hardening is a surface treatment by which the inside soft core of steel is hardened on the surface. Low carbon steels are case hardened because they cannot be hardened by quenching. The two step process involves carburizing followed by hardening. *Carburizing* involves heating the mild steel article surrounded by pieces of charcoal in a cast iron box to about 900° C for a sufficient length of time (about 3-4 hours) to allow for the adsorption of carbon on the surface of the article to the required depth of about 0.08-1.5 mm. The outer skin of the article is converted to a high carbon steel containing 0.8–1.2% of carbon. *Gas carburizing* is a method of heating the mild steel article in the presence of gases rich in hydrocarbons (e.g.,coal gas) to surface harden the material. The carburized steel is then *hardened* in the second step by heating to 900° C and quenching in oil followed by re-heating to about 700° C and quenched in water. The outer surface of the article is hardened by this treatment.

Nitriding produces a hard surface on alloy steels. The process involves heating the alloy in the presence of ammonia to about 550° C. Ammonia decomposes and the nitrogen formed combines with alloying elements to form hard nitrides on the surface of the alloy.

Cyaniding also produces case hardened medium carbon steel articles. The article is immersed in a molten bath of sodium or potassium cyanide at about 850° C for some time to facilitate the adsorption of both carbon and nitrogen and then quenched in oil or water.

Solved Examples

1. Apply phase rule to calculate the (a) the degrees of freedom at triple point and for the phase equilibrium $S_R = S_V$; (b) the number of phases in the equilibrium $MgCO_3(s) = MgO(s) + CO_2(g)$ and (c) for the thermal decomposition of $NH_4Cl\ (s) = NH_3(g) + HCl\ (g)$; and the number of components in
$H_2O(l) = H_2(g) + \frac{1}{2} O_2(g)$
and Ag(s) in equilibrium with Pb + Ag liquid.

Solution:

(a) F at triple point = C – P + 2 = 1 – 3 + 2 = 0
(Since C = 1 and P = 3)

F for the $S_R = S_V$ equilibrium 1 – 2 + 2 = 1
(Since C = 1 and P = 2)

(b) No. of phases in $MgCO_3\ (s) = MgO\ (s) + CO_2(g)$
= 3
(two solid phases + 1 gas phase)

No. of phases in $NH_4Cl\ (s) = NH_3\ (g) + HCl\ (g)$;
= 2
(1 solid + 1 gas phase)

(c) No. of components in $H_2O(l) = H_2\ (g) + \frac{1}{2} O_2\ (g)$
= 1

No. of components in Ag(s) = Pb + Ag liquid = **2**

◆

2. A 10 kg of alloy of bismuth and cadmium contains 23% Cd. Calculate the mass of Bi in the eutectic if the eutectic composition contains 40% Cd and the mass of the eutectic solid.

Solution:

Cd content in 10 kg = 2.3 kg
and the Bi content = 7.7 kg

If the eutectic composition contains 40% Cd corresponding to 2.3 kg of Cd the mass of Bi in the eutectic = (2.3 × 60)/40 = **3.45 kg of Bi.**

Mass of eutectic solid = 2.3 + 3.45 = **5.75 kg**.

◆

3. A 100 kg molten alloy of lead-silver containing 0.15% of silver was cooled to form an eutectic with 2.6% silver. Calculate (a) amount of silver that can be recovered from the eutectic mass and (b) the mass of lead that separates out.

Solution:

Mass of silver in 100 kg of alloy in 0.15 kg.
Mass of silver in eutectic = (0.15/2.6) × 100
= **5.769 kg**
Mass of lead that separates out = 100 – 5.769
= **94.231 kg.**

◆

Review Questions

1. State the phase rule and explain the terms involved with suitable examples.
2. Discuss the application of phase rule for ice-water-water vapour system.
3. How are the different phases of the one-component sulphur system represented in the phase diagram? Give an account on the various transitions with the help of the phase diagram.
4. What is condensed phase rule?

5. Write a note on thermal analysis. How are the heating and cooling curves useful?
6. Discuss the temperature-composition diagram of completely soluble metals.
7. What is eutectic point? Discuss the characteristics of the eutectic point with specific reference to the bismuth-cadmium system.
8. Discuss the phase diagram of lead-silver system and its use in obtaining pure metals.
9. Explain the terms congruent and incongruent melting of alloys.
10. Discuss the phase diagram of the magnesium-zinc system.
11. What are solders? What is their use? How can you explain the formation of solders with the help of a phase diagram.
12. Write a note on copper-aluminum casting alloys.
13. Discuss in detail the phase transformations in pure iron.
14. What are interstitial solid solutions?
15. Discuss in detail the iron-carbon phase diagram and its relevance to the heat treatment of steel.
16. Explain the terms case hardening, normalizing, nitriding and cyaniding.

3

SOLID STATE

3.1 Introduction

Matter consists of an aggregate of molecules existing in three different states—solid, liquid and gas. Gases and liquids have no definite or permanent shape and take the shape of the container in which they are placed. A gas occupies the entire volume of the container while a liquid exhibits a surface limiting its volume. Both gases and liquids are sensitive to variations of temperature and pressure. Solids are the most complex form of a molecular aggregate, with a definite three-dimensional shape. Solids are relatively more dense, hard and strong in retaining their shape. The shapes of solids are relatively stable and are not affected much by changes in temperature or pressure. Solids exhibit a wide variety of physical and mechanical properties such as electrical and thermal conductivity, hardness, strength, toughness, etc. It is these characteristic features of solids that renders them useful for engineering applications of fabrication and construction under a variety of situations.

3.2 Amorphous and Crystalline Solids

Solid substances exist in two types (i) amorphous solids (ii) crystalline solids.

Amorphous solids resemble liquids in that, they do not have an ordered structure, i.e., an orderly arrangement of atoms or ions in a three-dimensional structure. These solids do not have a sharp melting point and the solid to liquid transformation occurs over a range of temperature. The physical properties exhibited by amorphous solids are generally isotropic as the properties do not depend on the direction of measurement and show the same magnitude in different directions or Cartesian axes. Glass is a good example of an amorphous solid which is quite rigid and incompressible. X-Ray diffraction studies on glass show concentric rings indicating that solid glass has a certain amount of order but not a completely ordered structure. The absence of the long-range order is also indicated by the breaking pattern of glass. Glass breaks into conchoidal shapes instead of cleaving into flat surfaces or faces with characteristic angles between faces. Other examples of amorphous solids include solid polymers and plastics.

Crystalline solids in general are characterised by their rigid and incompressible nature with sharp and high melting points. Many of the crystalline solids exhibit an anisotropic behaviour in their physical, optical, mechanical and electrical properties. Crystalline solids have a highly ordered arrangement of constituent atoms, ions or molecules in a three-dimensional layer or lattice, giving rise to distinct geometrical shapes. The external shape of a crystalline solid is called its *habit*. The habit varies depending on the conditions during the growth of the crystal. Thus sodium chloride crystallises in the form of cubes from an aqueous solution, but its habit can be modified into octahedral shape by the addition of a habit modifier such as urea. Addition of a trace of potassium ferrocyanide to brine modifies sodium chloride crystals into needles or dendrite type. Similarly raffinose naturally present in sugar beet modifies sucrose crystals to a cubic appearance at a concentration of about 1%, but at higher concentrations (~2%) it modifies sucrose crystals into thin plates.

3.3 Crystallography

Crystallography is the branch of science involving the study of the shape or geometry of crystals, their properties and internal structures. *Optical* or *geometrical crystallography* and *X-Ray crystallography* are the two major methods of study in vogue at present, the first method is used on the external morphology and the second method on the internal structure.

3.4 Optical Crystallography

Optical or geometrical crystallography involves the study of the external geometry of crystals by visual examination developed by geologists and mineralogists. All crystals show flat surfaces called *faces*, sharp *edges* formed by the meeting of two faces and *vertex* or *corner* at the intersection of three or more edges. The overall geometry or shape of the crystal can be described in terms of *polyhedra* arising out of a combination of faces, edges and vertices as given by the Descartes-Euler theorem, which states, that face + vertices = edges + 2. The application of the theorem to different polyhedra commonly found in crystals is shown in Table 3.1.

Table 3.1 Different polyhedra seen in crystals

Polyhedron	*Faces*	*Vertices*	*Edges*	*No. of faces meeting at the vertex*
Tetrahedron	4	4	6	3 triangles
Octahedron	8	6	12	4 triangles
Cube	6	8	12	3 squares
Icosahedron	20	12	30	5 triangles
Dodecahedron	12	20	30	3 pentagons

3.5 Laws of Crystal Structures

Geometrical crystallography resulted in the enunciation of laws of crystal structures in the form of: (i) constancy of interfacial angles: (ii) rationality of indices and (iii) symmetry.

3.5.1 The law of constancy of interfacial angles

The law states that, *the corresponding faces or planes forming the external surface of a crystal of a given substance always intersect at a definite angle which remains constant at a given temperature no matter how the face develops.* Thus, for example, all the interfacial angles of cubic sodium chloride crystals are found to be 90° independent of the size and shape of faces.

3.5.2 The law of rationality of indices

The law put forward by Abbe Haüy states that, *the ratio between intercepts on crystallographic axes for the different faces of a crystal can be expressed by rational numbers.* The law can be explained with the help of a plane *ABC* with intercepts along *OA*, *OB* and *OC* along the x, y and z axes at distances of $2a$, $3b$ and $3c$ respectively as shown in Figure 3.1. The coefficients a, b and c are known as *Weiss indices* of a plane.

Weiss indices happen to be whole numbers (2, 3 and 3 respectively) in the chosen case. However, they may have fractional values, as well as infinity and hence are inconvenient to use and have been replaced by *Miller indices*. Miller indices of a plane are obtained by taking the reciprocals of the Weiss indices and multiplying each reciprocal by the *LCM* of the denominator of the fractions to get integers. Taking the reciprocals of Weiss indices in the present example, 1/2, 1/3 and 1/3 and multiplying with 6 the integers 3, 2, 2 are obtained as Miller indices. The plane with the Miller indices 3, 2, 2 is designated as (322) plane and in general the planes are termed (*hkl*) planes.

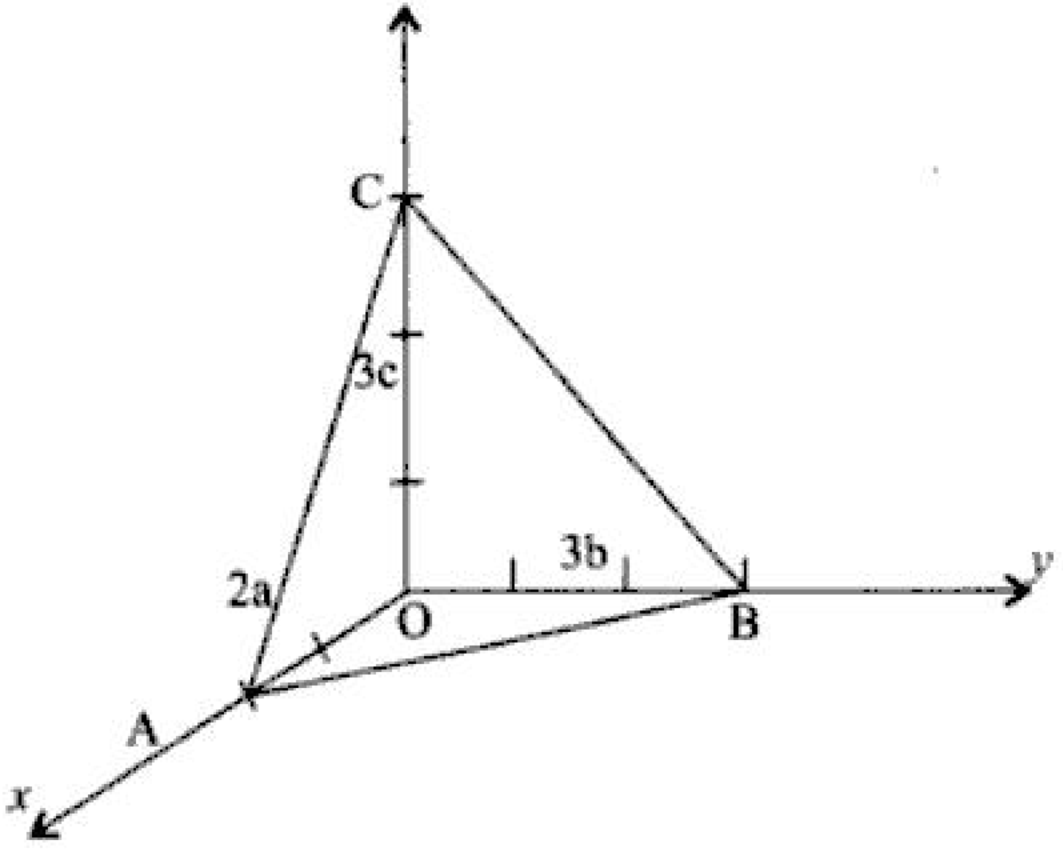


Fig. 3.1 Intercept of planes for calculating the rationality of indices

The relationship between the Weiss indices and the Miller indices of a few planes are given in Table 3.2

Table 3.2 Miller indices of a few planes

Weiss indices	*Reciprocals*	*Miller indices*
2,3,4	1/2, 1/3, 1/4	(643)
2,2,∞	1/2, 1/2, 0	(110)
∞,1, ∞	0, 1, 0	(010)
1, ∞,∞	1,0, 0	(100)

3.5.3 Elements of symmetry

Crystals can be classified into seven crystal systems on the basis of their external symmetry. Symmetry is an important aspect of molecular shape. The law of symmetry states that *all crystals of the same substance possess the same elements of symmetry*. A crystal may have one or more of the three types of symmetry. The elements of symmetry include the *plane of symmetry*, *axis of symmetry* and *centre of symmetry*.

The ***plane of symmetry*** is an imaginary plane which divides the crystal into two halves each of which is the mirror image of the other as shown for a cube in the Figure 3.2. A cube is a highly symmetrical geometric shape and has a total of nine planes of symmetry.

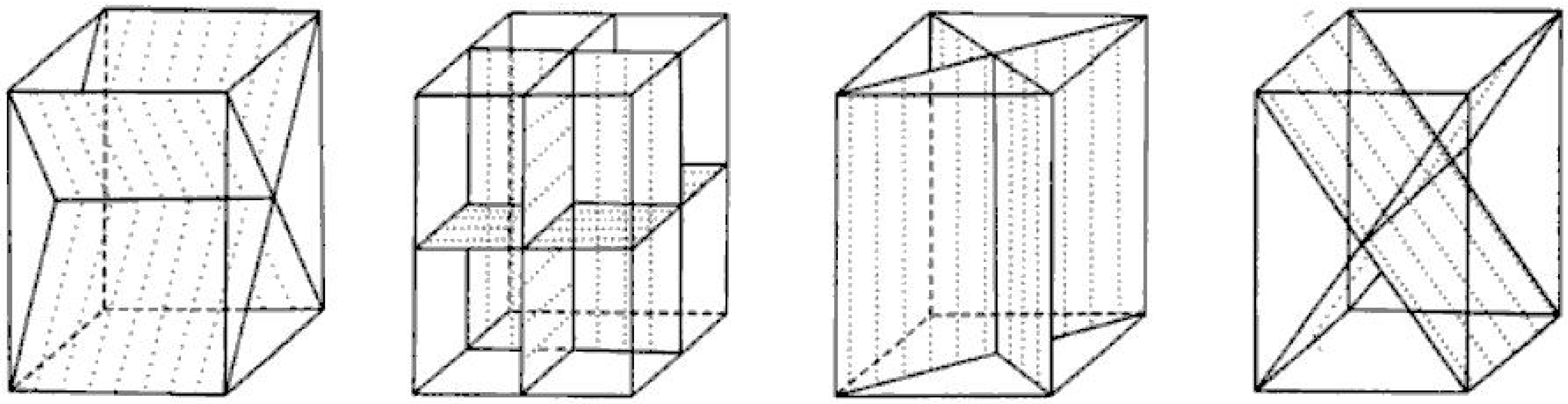


Fig. 3.2 Planes of symmetry in a cube

The ***axis of symmetry*** is an imaginary axis or line passing through the crystal. The crystal shows exactly the same appearance more than once during one complete rotation of 360° about this axis. A crystal is said to have an n-fold axis of symmetry when it presents an arrangement indistinguishable from the first on rotation about the axis through an angle of $360°/n$. The axes of symmetry with $n = 2, 3, 4$ and 6 are called two-fold (diad), three-fold (triad), four-fold (tetrad) and six-fold (hexad) respectively. Figure 3.3 shows some of the axes of symmetry for a cube. A cube has a total of 13 rotation axes consisting of 6 diad axes, 4 triad axes and 3 tetrad axes.

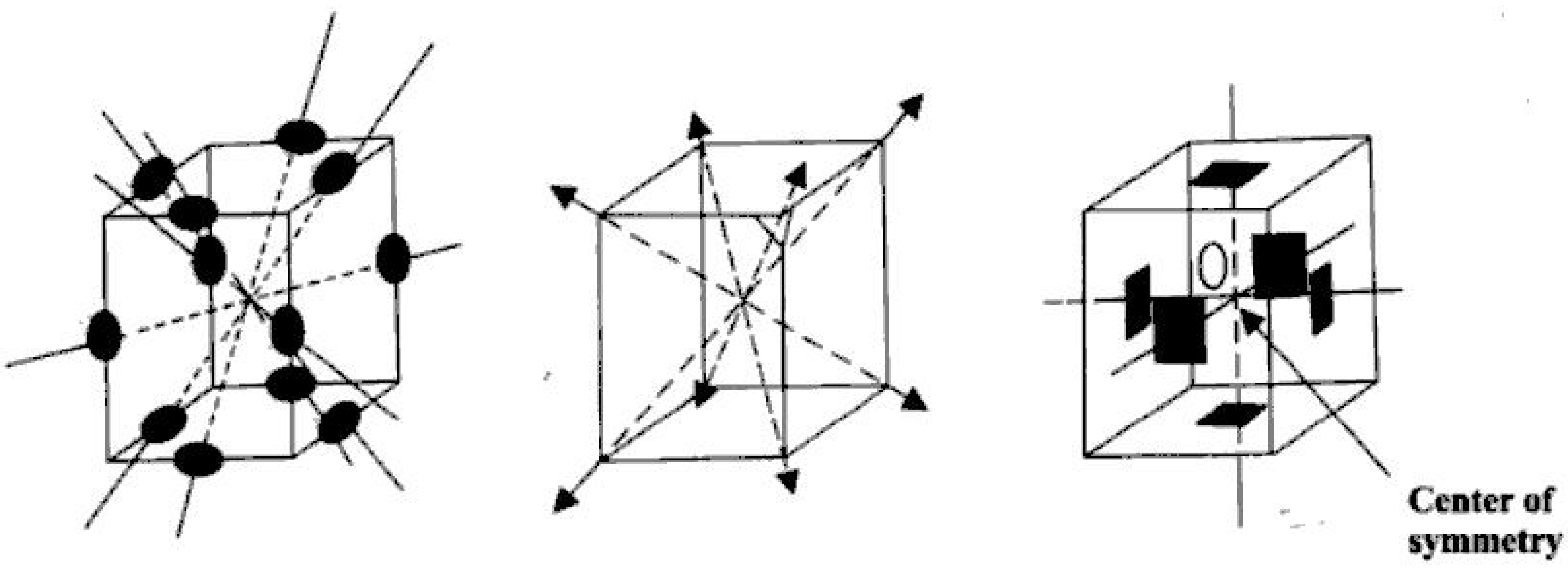


Fig. 3.3 Axes of symmetry in a cube

The ***centre of symmetry*** is a point within a crystal and if any line is drawn through the point it intersects the identical surfaces of the crystal at equal distances on either side of the point. A crystal can have only one centre of symmetry and all the planes of symmetry and axes of symmetry pass through this point. The centre of symmetry is also the ***inversion centre,*** because inversion of the crystal about this point results in an arrangement indistinguishable from the original one. The centre of symmetry in a cube is its body centre. A cube has a total of 23 elements of symmetry.

The procedure by which a body is brought into a position that is indistinguishable from its original position through the use of any of the symmetry elements is called a *symmetry operation*.

3.6 Crystal Systems

On the basis of symmetry, the 230 crystal forms (possible as well as observed), have been grouped into 32 classes and these, in turn have been grouped into seven crystal systems. Abbe Haüy pointed out that the external geometry of the crystals is due to the regular and ordered arrangement of the internal constituents of the crystal. Crystal geometry is best described in terms of crystallographic axes and the angles between the axes. The intercepts of the crystal faces on the crystallographic axes (length of the axes) and the angles of inclination between the axes, vary from system to system and are sufficient to describe all the known crystal forms. Table 3.3 lists the seven crystal systems and their characteristics.

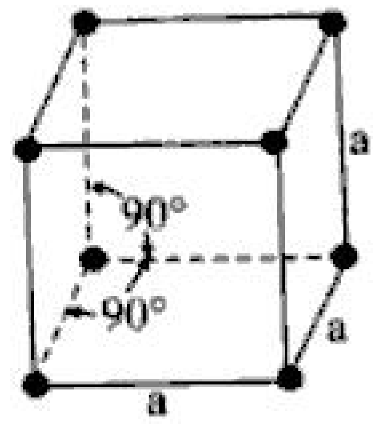
Table 3.3 Crystal systems and their characteristics

System	*Crystallographic elements*	*Essential Symmetry*	*Number of point groups*	*Examples*
Cubic	Axes $a = b = c$ Angles $\alpha = \beta = \gamma = 90^\circ$	4 triad axes 3 diad or 3 tetrad axes	5	NaCl, CsCl, ZnS, Cu, Ag, Au, diamond.
Tetragonal	Axes $a = b \neq c$ Angles $\alpha = \beta = \gamma = 90^\circ$	1 tetrad axis	7	Sn (white tin), SnO_2, TiO_2 (rutile)
Orthorhombic or rhombic	Axes $a \neq b \neq c$ Angles $\alpha = \beta = \gamma = 90^\circ$	3 diad axes or 1 diad axis and 2 perpendicular planes intersecting in a diad axis	3	α-S (rhombic), K_2SO_4, $BaSO_4$ TiO_2(brookite)
Monoclinic	Axes $a \neq b \neq c$ Angles $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	1 diad axis or 1 plane	3	β-S(monoclinic), $CaSO_4.2H_2O$
Triclinic	Axes $a \neq b \neq c$ Angles $\alpha \neq \beta \neq \gamma \neq 90^\circ$	No axes or planes	2	$CuSO_4.5H_2O$, $K_2Cr_2O_7$
Hexagonal	Axes $a = b \neq c$ Angles $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	1 hexad axis	7	Ice, graphite, Mg, Zn, Cd, HgS.
Rhombohedral or trigonal	Axes $a = b = c$ Angles $\alpha = \beta = \gamma \neq 90^\circ$	1 triad axis	5	$CaCO_3$(calcite), quartz, As, Sb, Bi, magnesite

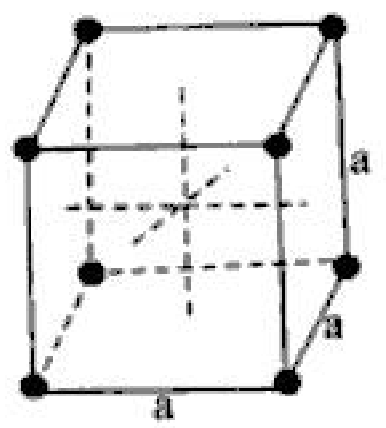
3.7 Crystal Structure

Geometrical crystallography is useful in identifying the crystals and their characteristics on the basis of external symmetry. However, the classification and characteristics of the crystals do not provide any information on the internal structure of the crystals. Crystallography postulates, that the internal structure of the crystal may be considered to be an ordered arrangement of the constituent particles in space. The constituent particles are considered as points called the *lattice points* and the imaginary planes containing the lattice points are called *lattice planes*. The regular three-dimensional arrangement of the lattice points in space is called the *space lattice*. The crystal of a substance is built up by repetition and extension in all directions of a fundamental structural unit called the *unit cell*, which has the same shape and symmetry as the entire crystal. The unit cell may be defined as the smallest repeating unit in three dimensions which represents the entire crystal. The crystal is considered to consist of a large number of such unit cells, each one in direct contact with its nearest neighbours and all are similarly oriented in space. Thus, if the crystal is a cube the unit cell will have its constituents arranged so as to give a tiny cube.

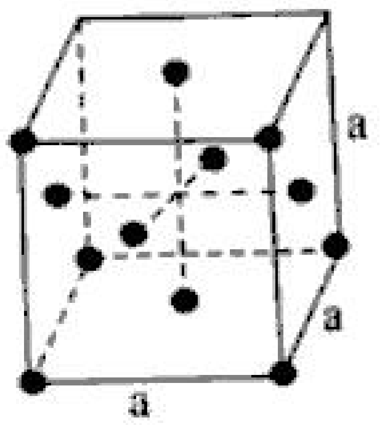
On the basis of mathematical analysis of three dimensional networks of points combined with the fundamental laws of crystallography, Bravais (1848) showed that there are only 14 basic arrangements of space lattices in which the similar points can be arranged in a regular pattern in a three dimensional space. The 14 *space lattices* or *Bravais lattices* are related to the seven crystal systems and subdivided into four types: (i) the primitive lattice (P-type) has lattice points only at corners; (ii) body-centred lattice (I-type – German – Innenzentrierte = in the centre) has a lattice point at the body centre also; (iii) face-centred lattice (F-type) with lattice points at the centre of all faces also and (iv) C-type lattice which has lattice points at the centres of a pair of opposite faces (end centred). The Bravais lattices for the seven crystal systems are shown Figure. 3.4.



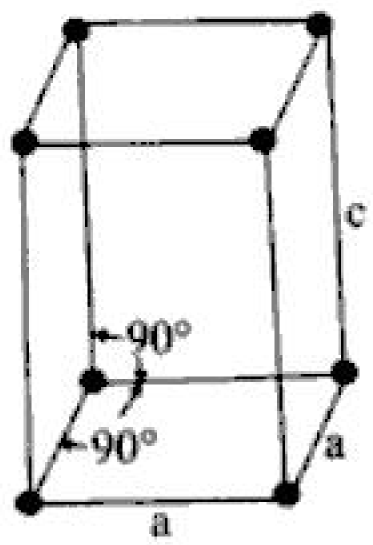
Simple
Cubic



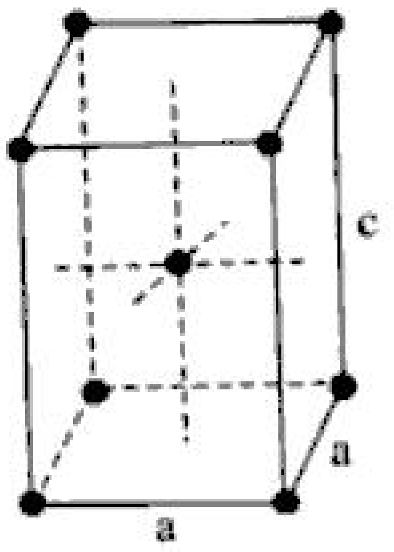
Body-centered
Cubic



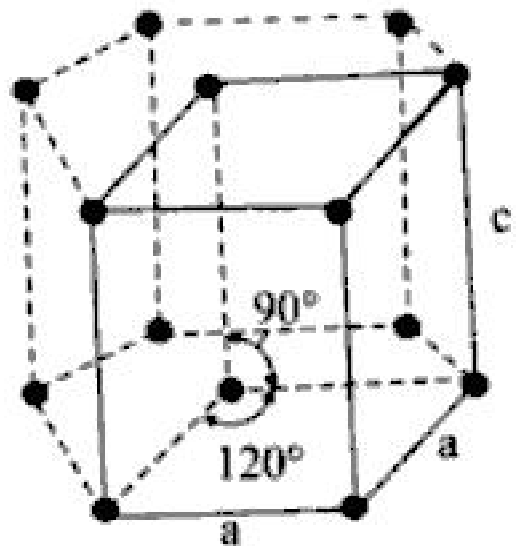
Face-centered
Cubic



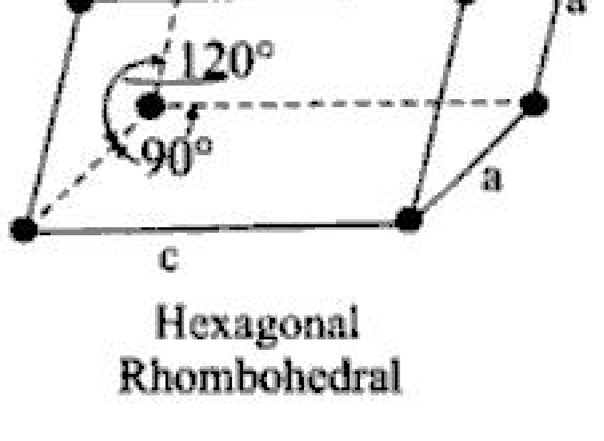
Simple
Tetragonal



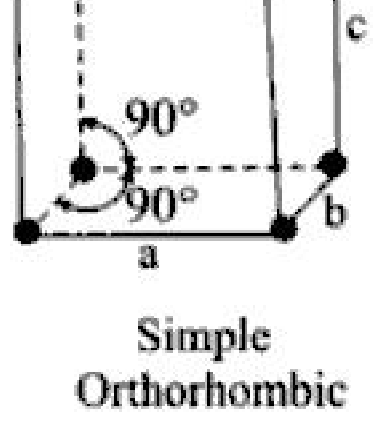
Body-centered
Tetragonal



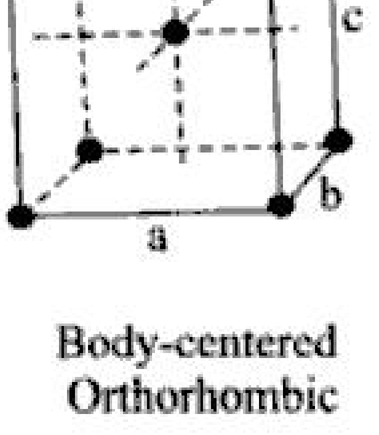
Hexagonal



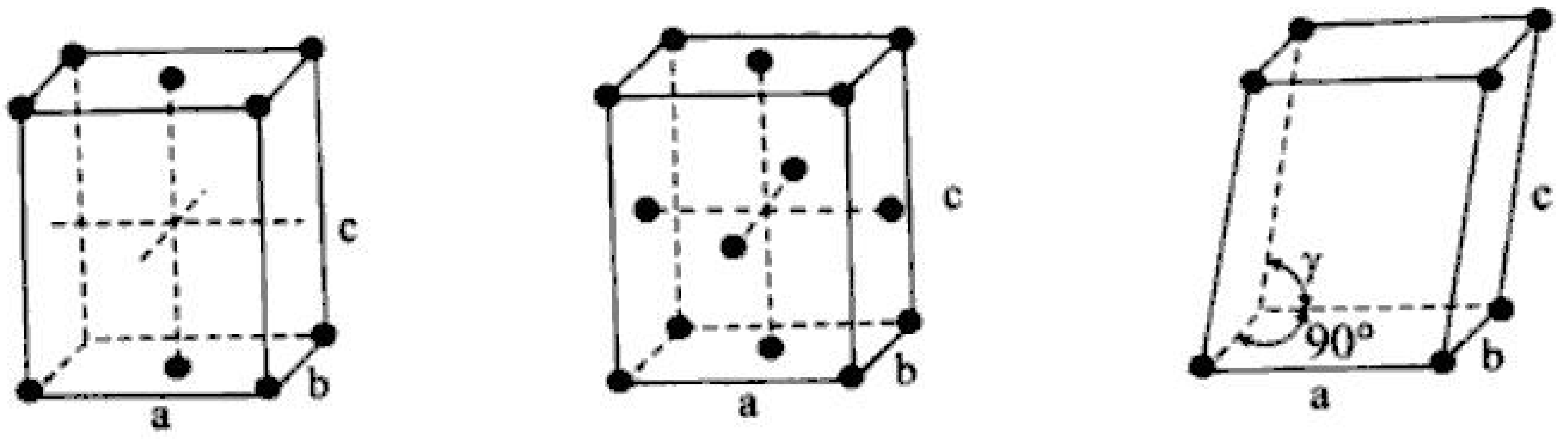
Hexagonal
Rhombohedral



Simple
Orthorhombic



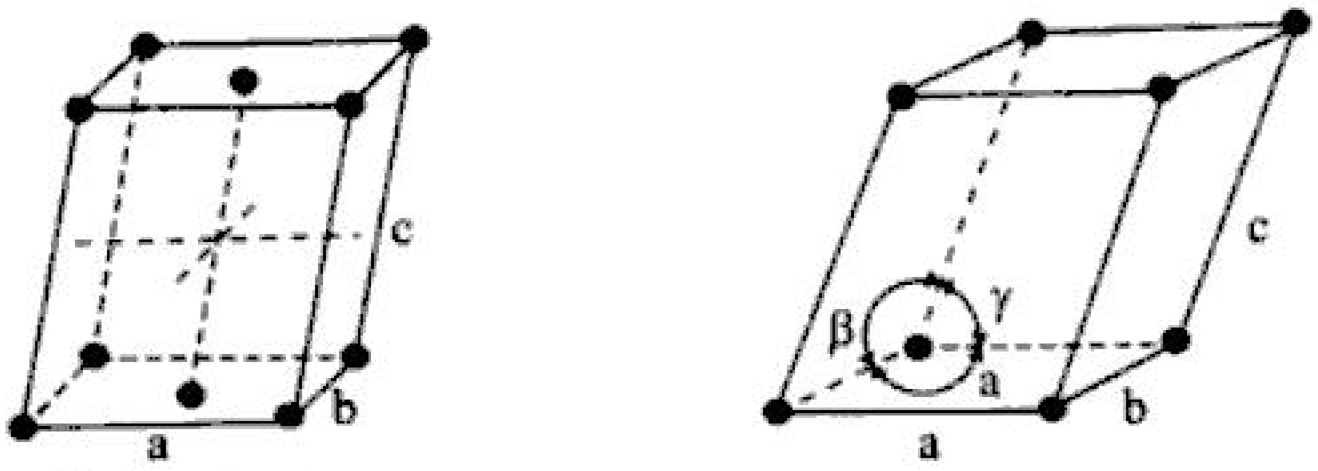
Body-centered
Orthorhombic



End-centered Orthorhombic

Face-centered Orthorhombic

Simple Monoclinic



End-centered Monoclinic

Triclinic

Fig. 3.4 Bravais lattices of seven crystal systems

Point group is defined as the distribution of the elements of symmetry about a single point in space and there are 32 ways of distribution (point groups). These point groups in conjunction with the 14 Bravais lattices gives rise to 230 more intricate groupings called *space groups*. The number of points or atoms in one unit cell is determined on the following basis: (i) atoms at a corner of a unit cell are shared between eight adjacent cells and hence only one-eighth of an atom is contributed to a single unit cell; (ii) atoms on a face are shared by two adjacent faces and only half of the atom is present in a unit cell; (iii) atoms on edge are shared by four adjacent cells and hence only one-fourth of the atom is taken in accounting for the unit cell and (iv) an atom within the cell is not shared and belongs to the unit cell.

The distances between parallel planes in a crystal are designated as *interplanar distance* and given the symbol d_{hkl}. For a cube, the interplanar distance is calculated from the values of the unit cell length (a) and Miller indices (hkl) using the formula

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \tag{3.1}$$

The determination of interplanar spacing is useful in the identification of whether the cubic lattice is of P-type, bcc or fcc type on the basis of the ratios of the interplanar spacings for the 100, 110 and 111 planes. The ratios are different for the three different types of cubic lattices. The P-type lattice has a ratio $d_{100} : d_{110} : d_{111}$ as 1: 0.707 :0.577 while the bcc type lattice has a ratio of 1 : 1.414: 0.577 and the fcc type has a ratio of 1 : 0.707 :1.154 for the same set of planes. The different planes in the cubic lattices are shown in the Figure 3.5. The interplanar spacings of a crystal can be determined by X-Ray diffraction as shown by Bragg.

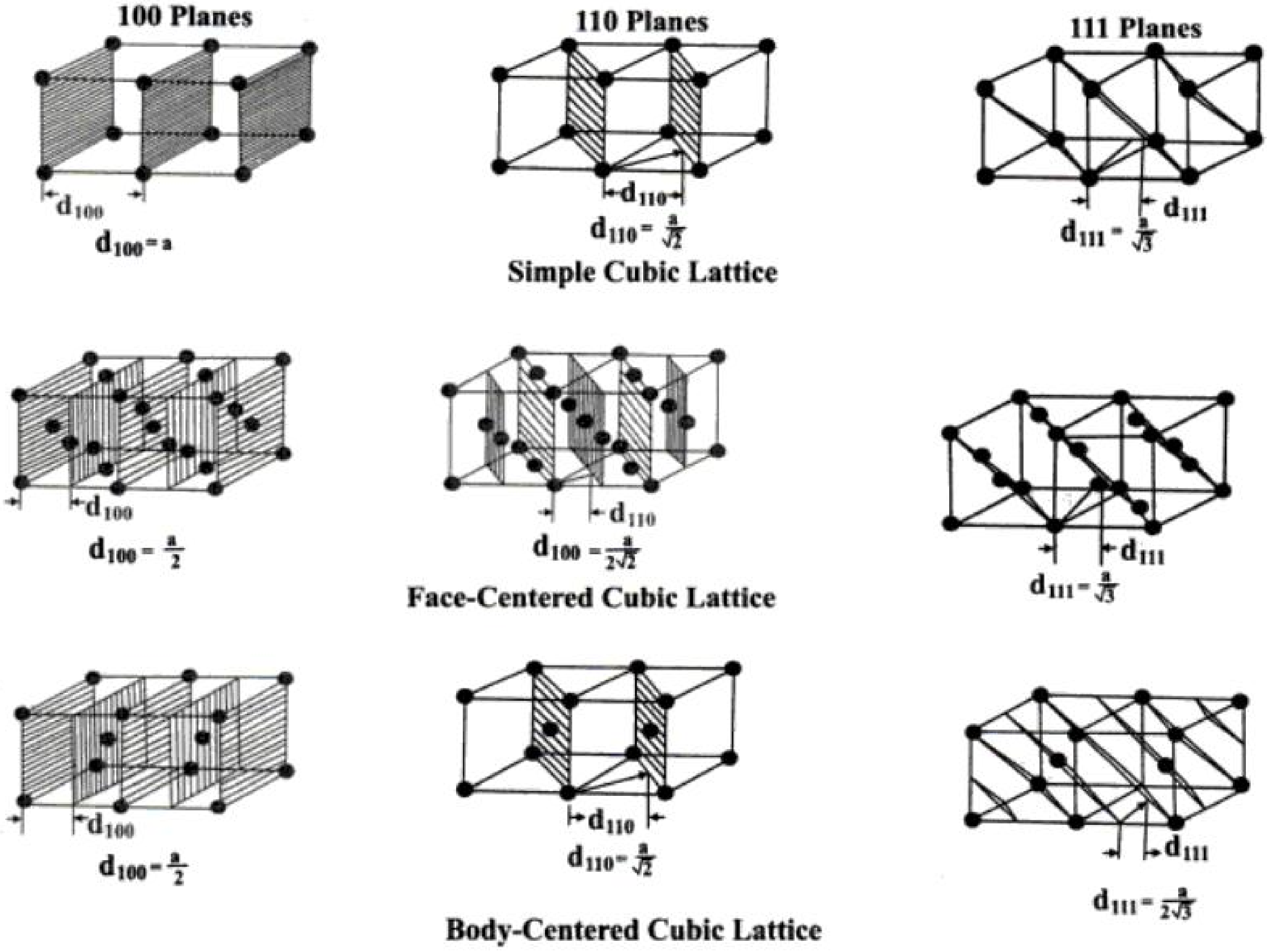

100 Planes
110 Planes
111 Planes
d_{100}
$d_{100} = a$
d_{110}
$d_{110} = \frac{a}{\sqrt{2}}$
Simple Cubic Lattice
d_{111}
$d_{111} = \frac{a}{\sqrt{3}}$
d_{100}
$d_{100} = \frac{a}{2}$
d_{110}
$d_{100} = \frac{a}{2\sqrt{2}}$
Face-Centered Cubic Lattice
d_{111}
$d_{111} = \frac{a}{\sqrt{3}}$
d_{100}
$d_{100} = \frac{a}{2}$
d_{110}
$d_{110} = \frac{a}{\sqrt{2}}$
Body-Centered Cubic Lattice
d_{111}
$d_{111} = \frac{a}{2\sqrt{3}}$

Fig 3.5 Planes in cubic lattices

3.8 X-Ray Crystallography

The crystal is made up of regular or ordered arrays of atoms in layers (lattice) and when an electromagnetic radiation passes through such a regular array it produces a diffraction pattern. It is possible to calculate the repeat distance or the interplanar distance of the regular arrays from the known value of the wavelength of the incident radiation and experimentally measured value of angle of diffraction. Since, for producing a diffraction pattern with crystals where the interplanar distances are in the order of a few Angstroms (10^{-8} cm),Von Laue suggested that X-Rays with wavelengths shorter than the interplanar distances be used for diffraction. The *Laue pattern* of diffraction produced by using polychromatic (different wavelength) x-radiation of ZnS crystal was difficult to interpret. The difficulty was overcome by the use of homogeneous or monochromatic x-radiation.

3.8.1 Determination of crystal structure

According to W.H.Bragg and W.L.Bragg (father and son respectively) crystals made of a series of equally spaced atomic planes may be used as reflecting gratings (instead of as transmission gratings used by Laue) and the diffraction pattern of X-Rays from crystals can be interpreted in terms of interference between X-Ray beams reflected from the various lattice planes. They also suggested the use of X-Rays of uniform wavelength (monochromatic radiation). A parallel beam of monochromatic X-Rays approaching at an angle, a series of parallel equidistant atomic planes x, y, z etc. of a crystal gets reflected as shown in the Figure 3.6. A part of the beam gets reflected from the point *B* along *BC* and another part of the beam gets reflected similarly at the next plane of atoms along *EF*. The two reflected X-Ray beams will interfere constructively giving rise to a diffraction maximum, if only the path difference between them is a whole number of the incident wavelength.

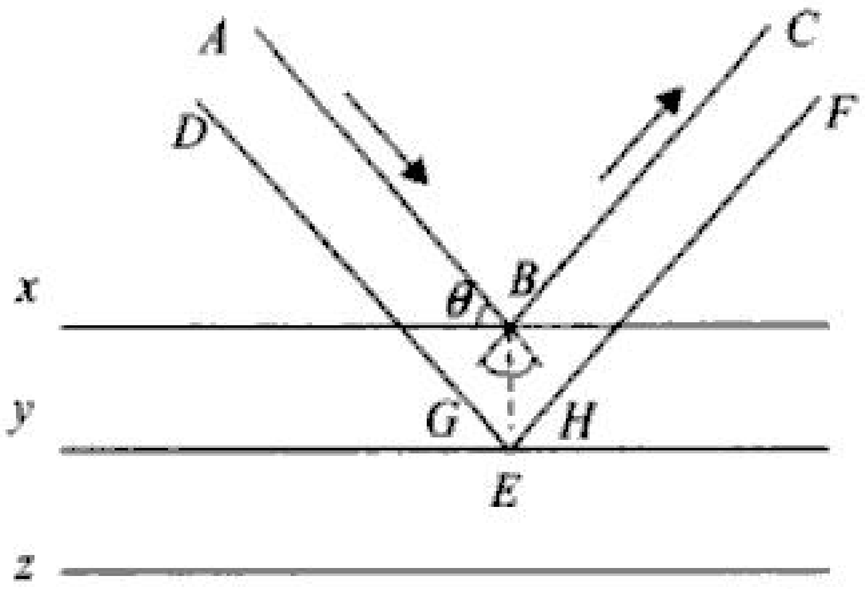


Fig. 3.6 Reflection of X-Rays by parallel planes of a crystal

The path difference between the two reflected beams is equal to $(GE + EH)$. The angle GBE = angle $EBH = \theta$, $GE = EH = d \sin \theta$ and the path difference $= 2d \sin \theta$. The condition for constructive interference and diffraction maximum is given as

$$2\, d \sin \theta = n\, \lambda \tag{3.2}$$

This equation is known as the Bragg equation, and *n* is called the order of reflection. The condition of constructive interference depends on the angle θ because for monochromatic x-radiation, the wavelength λ is constant, and for a given family of lattice planes, the interplanar distance *d* is also a constant. As the angle *θ* increases gradually, diffraction maxima occurs only for the integral values of *n* (1, 2, 3, etc.) and as *n* increases, the intensity decreases. Usually the reflections are assumed to be of the first order ($n = 1$). In the Bragg's method, a monochromatic beam of X-Rays is focused on the face of a single crystal mounted on a turn table and the reflected beam is allowed to pass into an ionisation chamber (detector). The detector's response is proportional to the intensity of the x-radiation entering the dectector. The ionisation chamber and the turn table rotate about a common axis. The ionisation chamber rotates through twice the angle through which the crystal face is rotated to ensure the reflected beam from all glancing angles enters the detector. The intensity of the reflected beam is measured for the various values of *θ*, and the values of *d* for different (*hkl*) planes are calculated using the Bragg equation.

Bragg method requires the use of single crystals which are difficult to prepare. Hence *powder method* also known as the *Debye-Scherrer method* is widely used for substances which are not obtained as single crystals. In this method a powdered sample is exposed to a beam of monochromatic radiation and the reflected beam is allowed to enter the detector. The powder is polycrystalline and the crystallites are oriented at random and some of them will have their faces oriented at suitable glancing angles so as to satisfy the Bragg condition.

3.9 Structures of Crystalline Solids

X-Ray diffraction studies have indicated that many of the solids that occur in nature such as metals and others such as ionic compounds, covalent compounds, etc. have mostly crystal structures of fcc, hcp or bcc type. This observation is conveniently explained on the basis of *close packing of spheres*. Atoms are considered as space filling entities and three-dimensional structures can be built up by close packing of spheres in space so that the available space is filled efficiently. The concept was developed by assuming that the atoms of metals are hard spheres of identical size and later extended to even other solids consisting of constituent ions or groups of different sizes. The structure is built layer by layer. In the first layer (layer A in Figure 3.7) the best packing is achieved by having each sphere in contact with a maximum of six other spheres of identical size. A second layer (layer B) indicated by dotted circles is placed on top of the first layer by placing the spheres on the depressions of the first layer. The third layer (C layer) can be placed on the second layer once again in the depressions in the B layer so that the third layer is exactly placed above the A layer giving rise to a sequence of layers *AB,AB,AB, AB*.... etc. This sequence leads to an overall structure called *hexagonal close packing* (hcp) with a six-fold axis of symmetry (vide Figure 3.8 a) Alternatively the third layer may be placed in a different set of depressions available in the B layer so that the C layer is differently placed giving rise to a sequence of layers *ABC, ABC, ABC, ABC*.... etc. This sequence will lead to a *cubic close packing* (ccp) or *face-centred cubic* (fcc) arrangement as shown in Figure 3.8 b. In both types of structures the packing efficiency is 74% with only 26% of available space becoming void space. The bcc arrangement is based on a simple cube with a packing efficiency of only 68%.

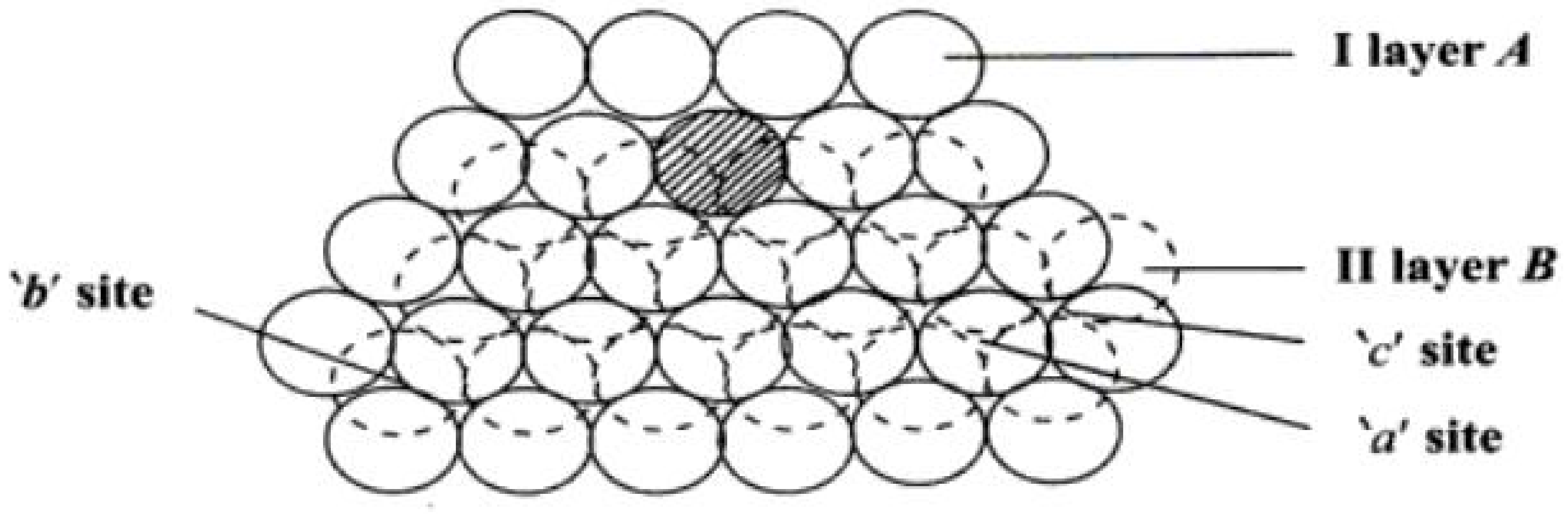
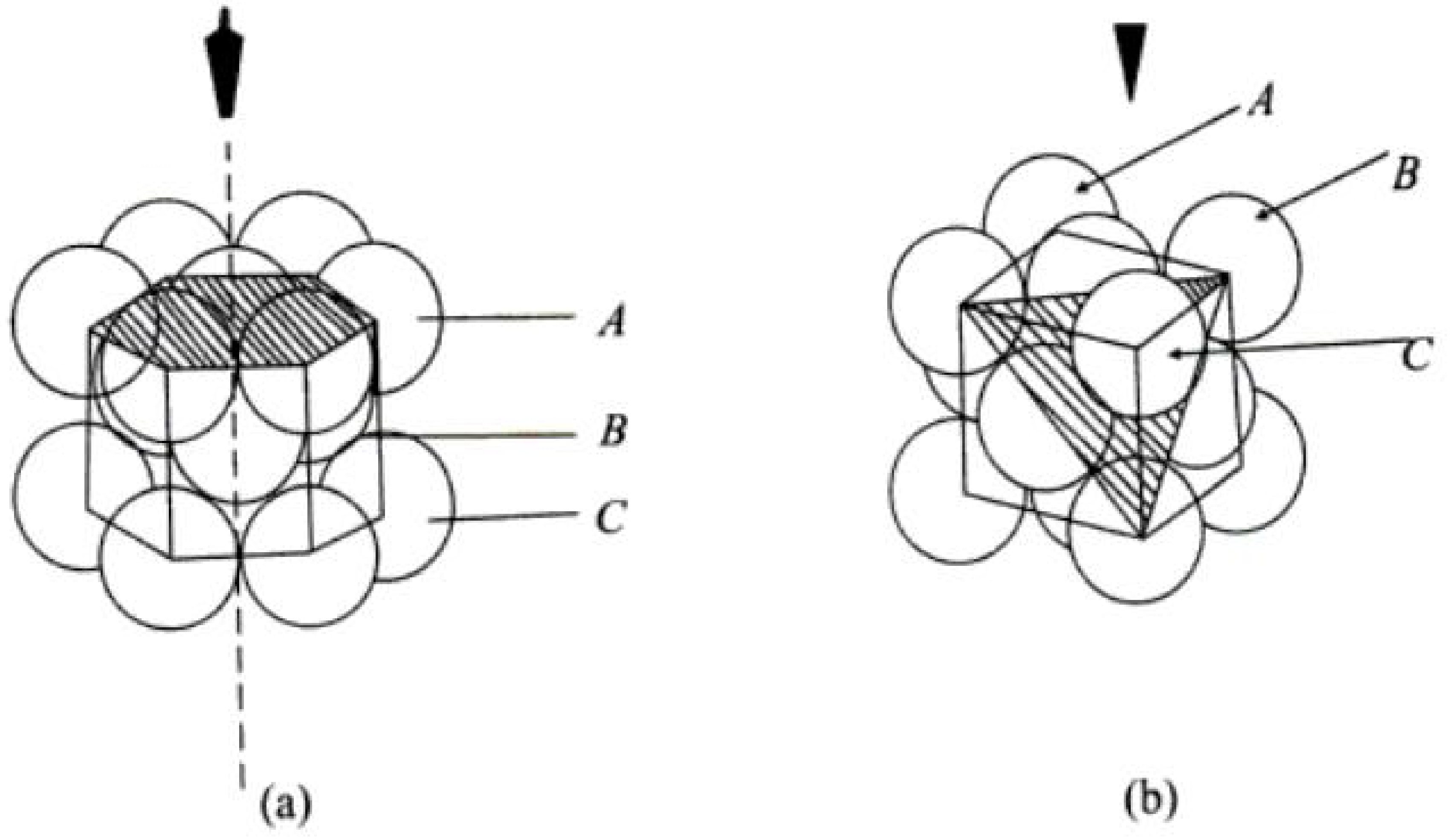


Fig. 3.7 Close packing of spheres



(a) (b)

Fig. 3.8 (a) Hexagonal close pack and (b) cubic close pack arrangements

3.10 Types of Crystalline Solids

Crystalline Solids may be broadly classified on the basis of the nature of binding forces involved into four main types, (i) metallic solids. (ii) ionic solids (iii) covalent solids and (iv) molecular solids.

3.11 Metallic Solids

X-Ray diffraction studies have revealed that metals have close packed structures. A large number of metallic elements crystallise in one of the three most efficient crystal lattices namely hcp, fcc, or bcc lattices. For example, elements crystallising in the hcp crystal structure include *s*-and *p*-block metals like beryllium, magnesium, zinc, cadmium and transition elements like osmium, ruthenium, yttrium, titanium, zirconium, cerium and chromium. Metals crystallising in the fcc lattice include coinage metals like copper, silver, gold, the alkaline earth metals calcium and strontium, and transition elements of scandium, lanthanum, iron, cobalt, nickel, rhodium iridium, palladium and platinum. Alkali metals, and transition elements α-iron, titanium, zirconium, hafnium, chromium, molybdenum, tungsten, vanadium and niobium crystallise in the bcc lattice.

Metals have only a weak tendency towards a directed covalence and hence metal atoms tend to pack together efficiently. An important consequence of this close packing is that metals often have high densities. The lack of directional characteristics of bonds also accounts for the wide occurrence of polymorphism under different conditions of temperature and pressure. For example, iron shows the polymorphic modifications as a function of temperature (see section 2.11). The structural features and bonding characteristics of metals is conveniently discussed in terms of band theory.

3.11.1 Band theory of metallic solids

Band theory of solids is mostly applicable to metals and alloys and is useful for explaining the metallic properties such as thermal and electrical conductivities. The theory may be considered as a modified molecular orbital theory extended to metallic solids in which the solid is treated as a large molecule. The theory is also called 'tight binding approximation' in solid state physics. The theory has been extended to even non-metallic solids (covalent and ionic solids) to explain the electrical properties.

The theory postulates that the metal lattice, consists of close packed atoms with the valence shell electrons of the atoms enveloping the entire lattice. The overlap of a large number of atomic orbitals of valence shell leads to the formation of molecular orbitals that are closely spaced in energy, and hence form a continuous *band* which covers a range of energies (Figure 3.9). The band consists of a group of closely spaced energy levels extending throughout the solid.

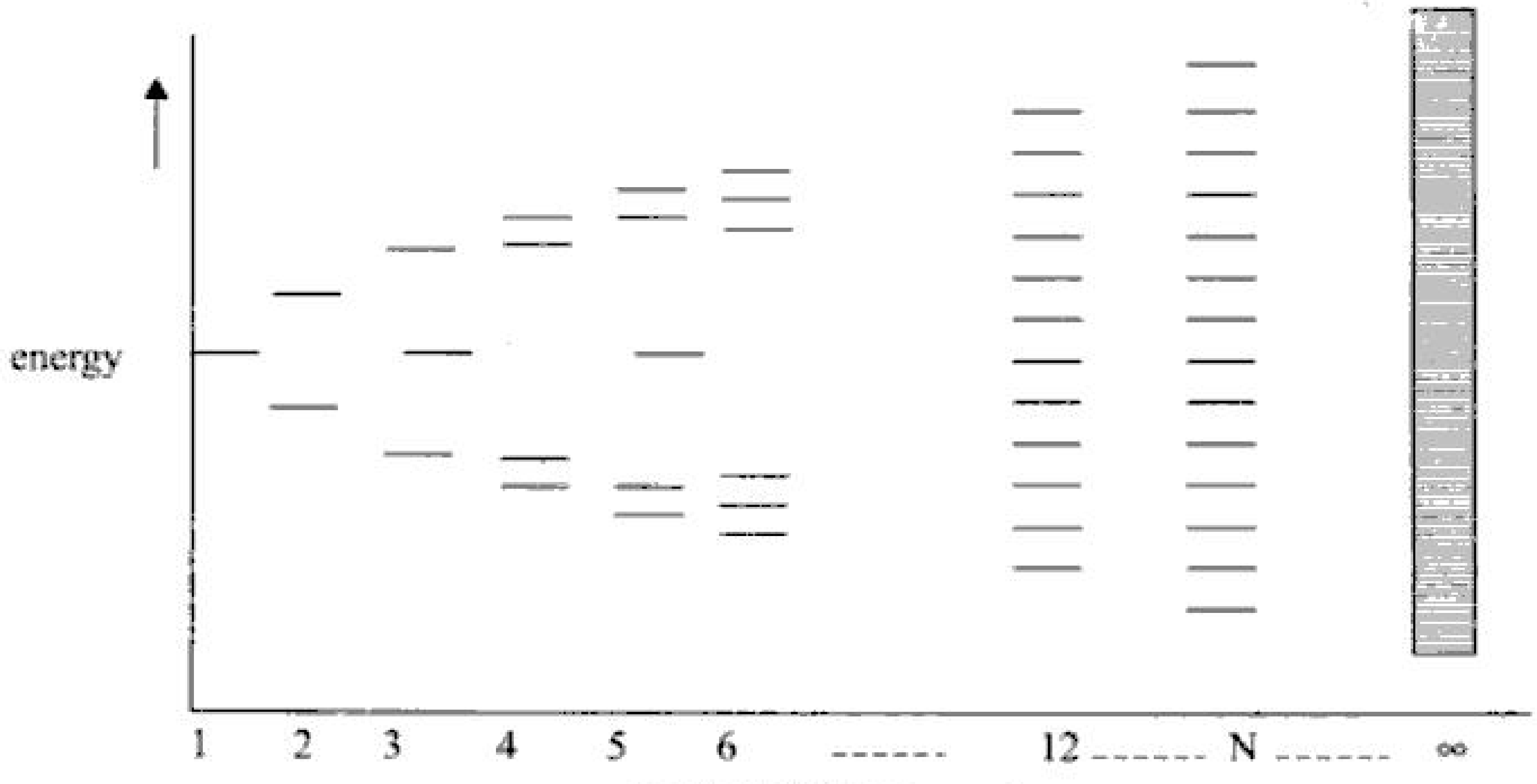


Fig. 3.9 Formation of continuous band in a large number of atoms

Overlap of the *s* orbitals of a large number of atoms results in an *s band* and similarly, the overlap of *p* orbitals results in a *p band.* Since the *p* orbitals are of higher energy as compared to *s* orbitals of the same valence shell, the *p* band is often separated from the *s* band by an energy gap called the *band gap* as shown in Figure 3.10 a. In sodium with an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^1$ the *s band* and *p band* are formed by the overlap of the 3s orbitals and 3p orbitals respectively. The inner core electrons do not participate in the band formation. The lower energy *s* band is half filled (as each molecular orbital can hold 2 electrons but only 1 electron is available in sodium) and called the *valence band* (VB). The higher energy *p* band is vacant and called the *conduction band* (CB). In the case of metals the valence band and the conduction band overlap and the band gap does not exist (Figure 3.10 b). The migration of electrons from the lower energy levels to the vacant higher energy levels of the valence band or to the vacant conduction band gives rise to electrical conductivity. Electrical conductivity of metals is quite high as the electrons can easily cross-over to the conduction band in the absence of a band gap.

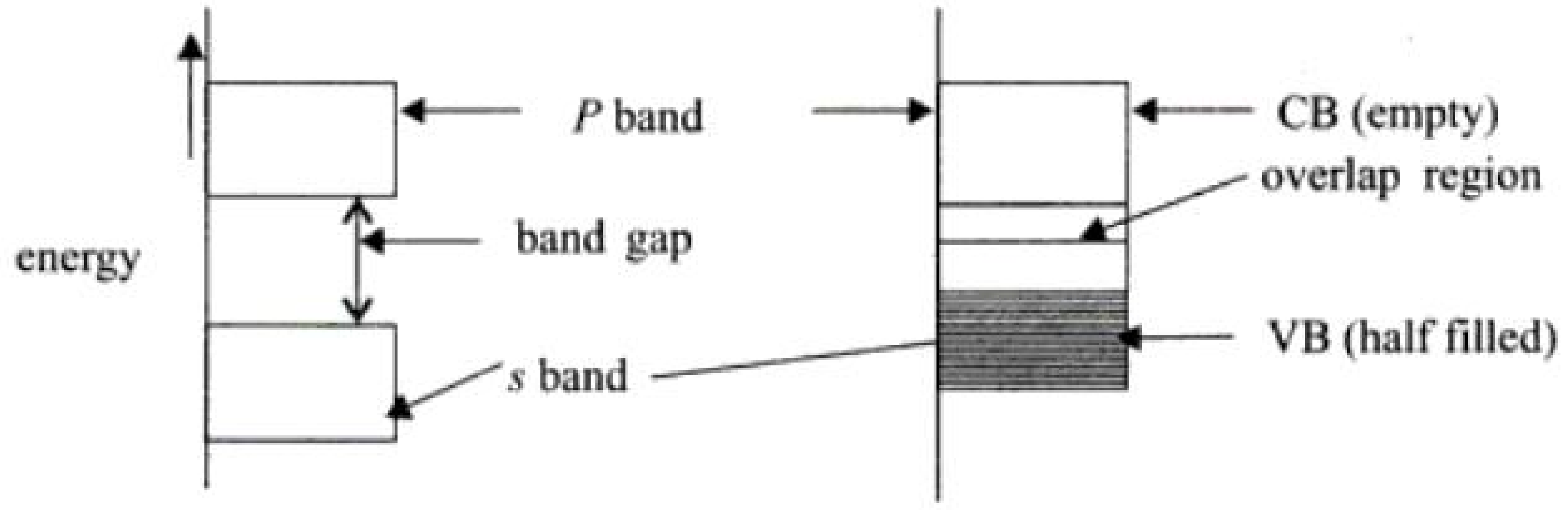


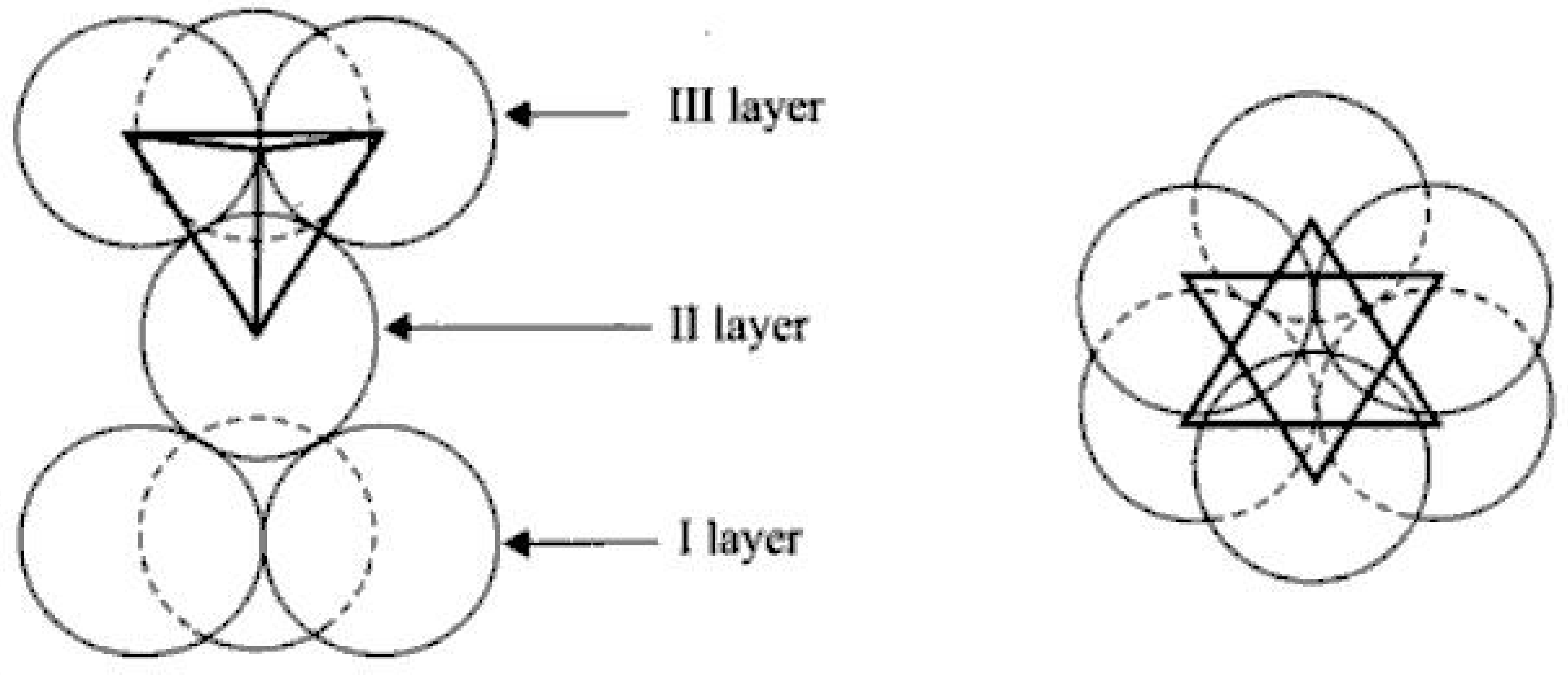
Fig. 3.10 (a) *s* and *p* bands of a solid (b) band structure in sodium

3.12 Ionic Solids

Ionic solids are mostly crystalline consisting of an assembly of cations and anions in an orderly arrangement of a three dimensional lattice. The binding forces are predominantly coulombic in nature. Both electrostatic attractions as well repulsions are responsible for holding the lattice. The percent ionic character of the 'bond' is large when the electronegativity differences between the combining atoms is large as in the case of highly electropositive metals such as an alkali and alkaline earth metals and highly electronegative elements such as fluorine, chlorine, oxygen and to some extent sulphur. Ionic solids in general have high melting points and are brittle in nature. They do not conduct electricity in the solid state but their melts and aqueous solutions do conduct electricity due to the migration of charge carrying species.

3.12.1 Crystal structures of ionic solids

The crystal structures of ionic solids are also related to close packed arrangements. In the case of metallic elements, all the spheres representing the atoms of the same element have the same size. However, in ionic solids involving two different elements as in the case of binary solids, such as *Na*Cl, *Cs*Cl, *Ca*F_2, TiO_2, etc. the sizes of the spheres representing the atoms of two different elements are different, the anion being much bigger compared to the cation. The spheres cannot fill the whole space and leave void spaces called interstitial sites or holes. Two types of interstitial sites can be distinguished based on the number of spheres surrounding the void space; (i) a *tetrahedral site* and (ii) *octahedral site.* The tetrahedral site is named on the basis that four spheres enclosing the void space are at the corners of a regular tetrahedron with one sphere resting on the void space formed by three spheres in an adjacent plane. Each sphere is associated with two tetrahedral sites in a close packed arrangement, since the same sphere can rest on the void space formed by three spheres from the top layer or bottom layer as shown in Figure 3.11a.



(a) (b)

Fig. 3.11 (a) Tetrahedral site and (b) octahedral site in a close packed arrangement

An octahedral site (Figure 3.11 b) is formed by two sets of three spheres in adjacent layers. Each set of three spheres forms an equilateral triangle in parallel planes, the apices of the two triangles formed by the two sets of spheres pointing in opposite directions. Each sphere is associated with one octahedral site. The number of tetrahedral sites is twice the number of octahedral sites. The tetrahedral site being smaller in size can accommodate only the smaller sized atoms or ions as compared to the octahedral site.

The structures of ionic solids may be considered as a close packed arrangement of the larger sized anions with the smaller cations occupying the octahedral or tetrahedral sites. If all the available octahedral sites in the close packed arrangement of anions (A) are occupied by cations (B), the stoichiometry of the compound is AB and if only half the available octahedral sites are occupied the stoichiometry will be A_2B. Similarly, if all the available tetrahedral sites of the close packed arrangement of anions (A) are occupied by cations (B) the compound will have a stoichiometry of AB_2 and if half the available tetrahedral sites are occupied the stoichiometry will be AB. The crystal structures of such binary ionic solids are determined by two factors (i) the radius ratio r_c/r_a, where r_c and r_a represent the radii of the cation and anion respectively and (ii) the polarisation of anion by the cation leading to covalent bonding. Radius ratio is helpful in predicting the coordination number (the number of nearest neighbours) and the coordination geometry in an ionic solid. The coordination number depends on the relative sizes of the cation and anion and on the requirement that the central ion is in contact with all the neighbouring ions of the opposite charge so that the potential energy of the arrangement is minimum with the electrostatic attractive and repulsive forces balanced. A stable tetrahedral structure of four anions surrounding the central cation results (4-coordination) only when the central cation is in contact with all the four anions, the four anions remaining out of contact with each other. However if the cation becomes smaller in size, the cation occupying the tetrahedral site is rattling within the interstice and the anions will come into contact with each other enhancing repulsive forces and the structure is not stable. The critical radius ratio for a stable tetrahedral coordination is $r_c/r_a = (\sqrt{3} / \sqrt{2}) - 1 = 0.225$. Similarly the critical radius ratio

smaller as compared to that of the anion which results in a tetragonally distorted bcc arrangement of Ti^{4+} ions. Each cation is coordinated by 6 oxygen anions at the corners of an octahedron while each oxygen anion is coordinated by 3 cations at the corners of a plane triangle as shown in Figure 3.16.

The rutile structure is adopted by fluorides (MF_2) of manganese, cobalt, nickel, zinc and the oxides (MO_2) of manganese, ruthenium germanium, tin, lead and tellurium.

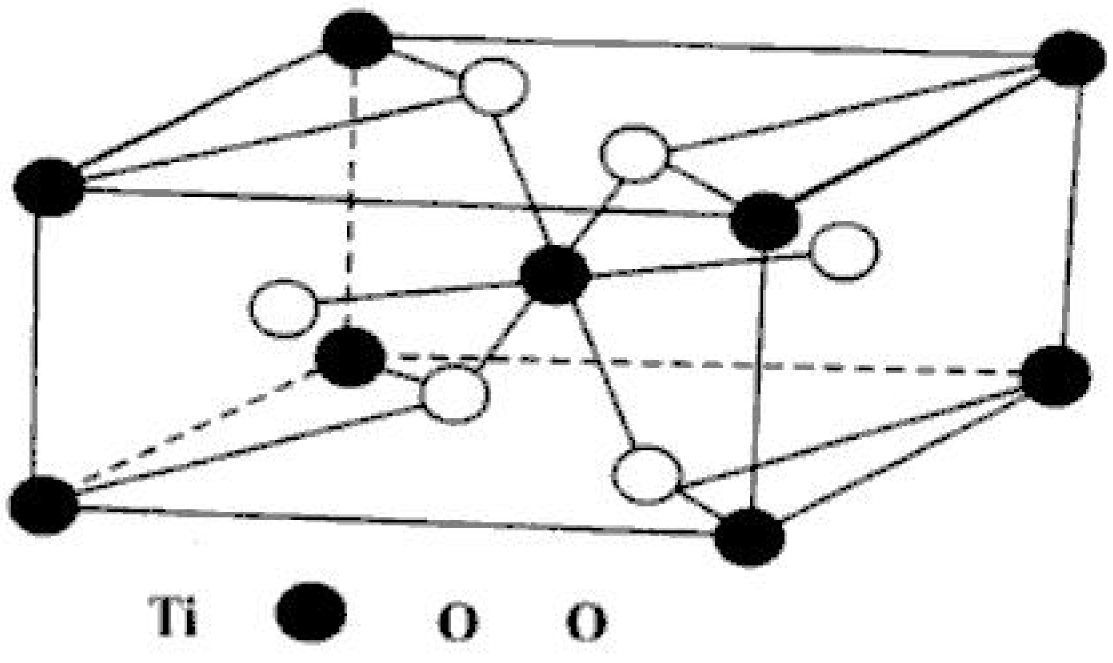
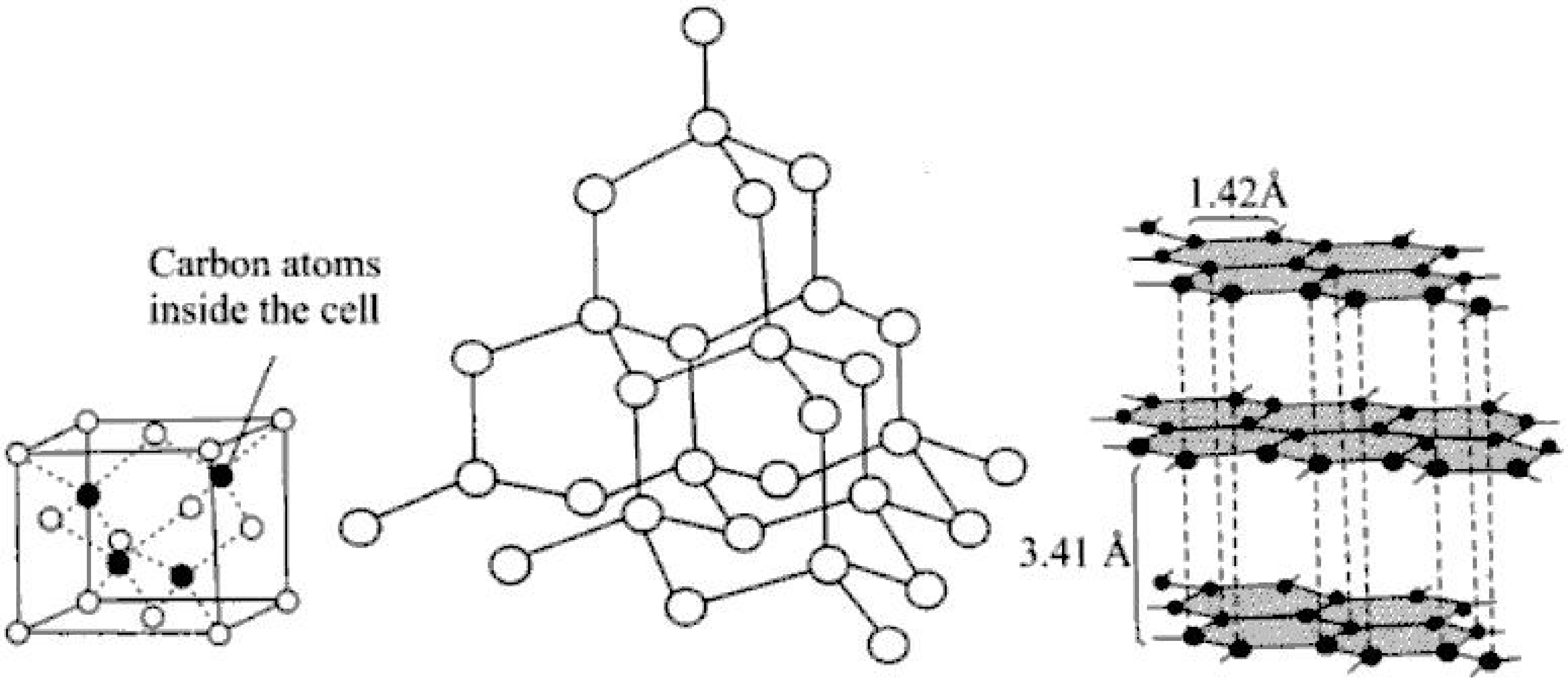


Fig. 3.16 Crystal structure of rutile

3.13 Covalent Solids

Covalent solids consist of combining atoms of the same element or of elements of similar electronegativities. The binding forces are predominantly covalent and give rise to three dimensional network structures. The solids are hard with high melting temperatures and mostly insulators. Examples of covalent solids mostly belong to the group IV elements of the periodic table and include diamond, graphite, silicon, germanium, grey tin and the covalent compounds of silicon carbide and borazon (BN). The maximum coordination number exhibited by the elements of the group IV is 4 and each atom is tetrahedrally coordinated by four others of the same kind.

The crystal structure of diamond, one of the allotropic forms of carbon, may be regarded as a giant molecule with each carbon atom covalently bound to four others extending throughout crystal. The strongly directed sp^3 hybridised bonds result in a relatively open bcc structure with only four of the eight cubelets occupied at the centres (Figure 3.17 a) rather than structures with a higher coordination.



(a) diamond

(b) graphite

Fig. 3.17 Crystal structure of diamond and the layer lattice of graphite

as Taylor dislocation) an extra half plane of atoms is inserted (or removed) along the slip plane in the lattice (Figure 3.23 a). The top plane of the lattice is displaced by one interatomic distance in a direction parallel to the slip plane so as to accommodate the inserted plane. The top portion of the crystal gets squeesed and distorted at the edges of the dislocation. The lattice retains its regularity farther away from the dislocation. Screw dislocation (also called Burgers dislocation) consists of a line of atoms with distorted coordination polyhedra brought about by displacement of a set of lattice planes relative to the neighbouring lattice planes (Figure 3.23 b). The displacement occurs by one or more lattice units in a direction parallel to the dislocation line. The properties of malleability and ductility exhibited by metals are attributed to these dislocations.

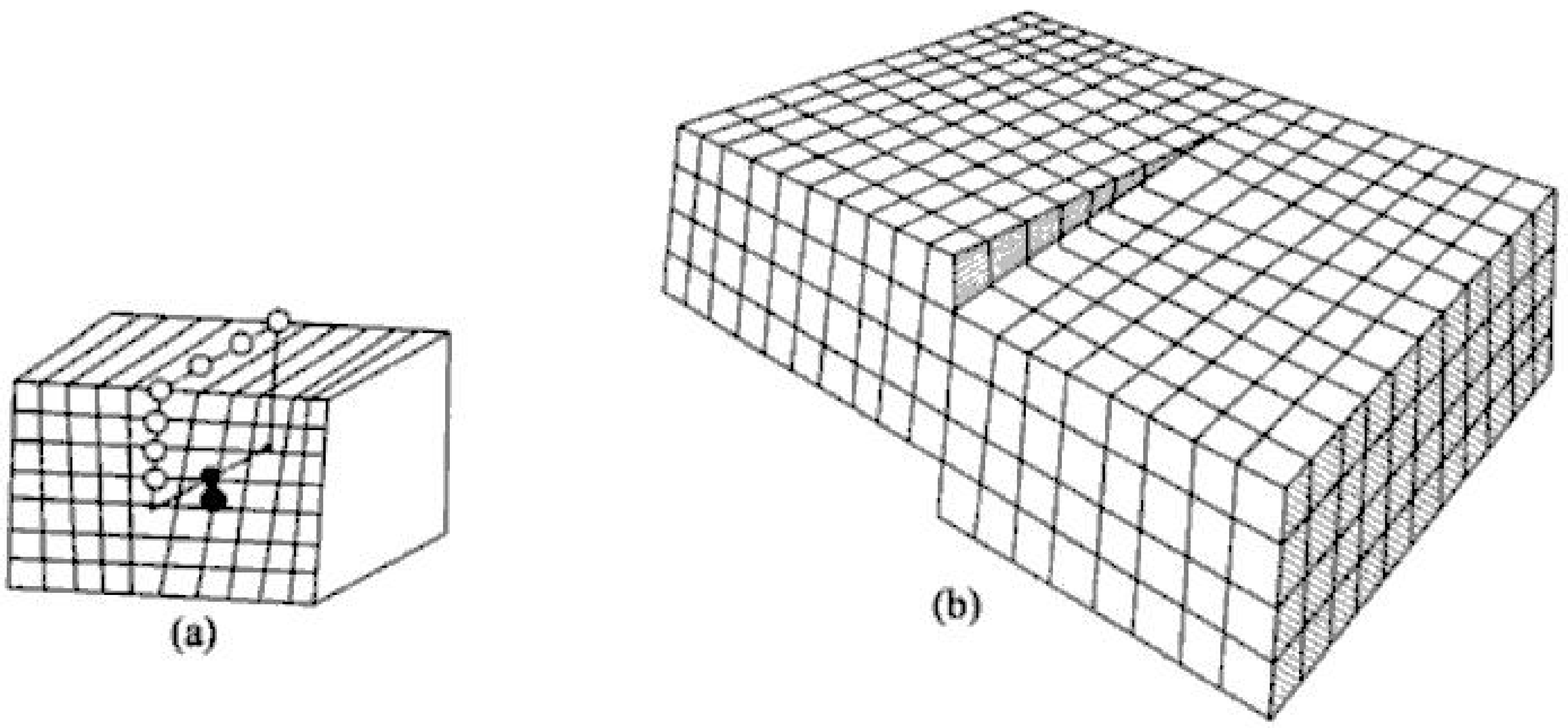

(a)
(b)

Fig. 3.23 Line defects in a crystal (a) edge dislocation and (b) screw dislocation

Plane defects include (i) slip of a plane (ii) twinning and (iii) surface defects

Slip is the large displacement of one part of the crystal relative to another part along certain crystallographic planes (slip planes or glide planes) and crystallographic directions (slip directions). More than one slip plane and slip direction exist in crystals. In a hexagonal close pack structure there are three slip directions while in fcc crystal there are twelve slip planes and slip directions because there are four families of parallel planes of maximum interplanar distance with three directions each per plane. Hence a fcc crystal is said to be highly plastic.

Twinning occurs during the growth of the crystal when atoms position themselves in a new orientation so that the latter grown part is not parallel to the earlier grown part of the crystal. The two parts are related to each other by a symmetry operation, which is a different symmetry operation possessed by the single crystal. For example in a single crystal of fcc the latter growing part of the crystal becomes a mirror image of the earlier grown part along the 111 plane though this plane is not a mirror plane in the fcc structure (Figure 3.24). The twins share a plane of atoms that fits right into the structure of each. A large number of twinned crystals occur in nature, e.g., gypsum, rutile, pyrites, hemimorphite, etc. Usually twinning and slip go together and twinning facilitates the slip.

Surface defects occur in polycrystalline solids and consist of differently oriented interlocking microcrystals. The individual crystals of different orientations are called *grains*. The grain boundary that separates the crystals of different orientations in the same crystal structure is a surface defect. The grain boundaries appear as lines when a metal is etched and observed by a microscope. Atoms in such regions are less stable and more reactive.

ionic solids electrical conductivity is mostly due to the migration of ions and hence they are called ionic conductors. Electrical conductivity in solids can be conveniently discussed in terms of band structures.

Solids are classified into *insulators*, *semiconductors* and *conductors*, on the basis of electrical resistivity which is conveniently explained by the band structure. Insulators have resistivities greater than 10^6 ohm-cm and the band structure consists of a completely filled valence band (VB) separated by a large band gap from a completely vacant conduction band (CB). Ionic and covalent solids are extremely poor conductors of electricity and are classified as insulators. Examples of ionic solids include alkali metal chlorides, fluorides and bromides such as sodium chloride, calcium fluoride and potassium bromide, metal oxides and metal sulphides. Covalent solids include diamond (carbon), silicon carbide, zinc sulphide, silver iodide, etc. Conductors have resistivities in the range 10^{-1} to 10^{-6} ohm-cm and the band structure consists of filled or partially filled valence band overlapping with the vacant conduction band. Metals and alloys are excellent conductors of electricity and are classified as conductors. Semiconductors have resistivities in the range 1 to 10^6 ohm-cm and the band structure consists of a filled valence band separated by a small band gap from the vacant conduction band. Examples of semiconductors include silicon and germanium. The band structures of the three types of solids are shown the in Figure 3.26.

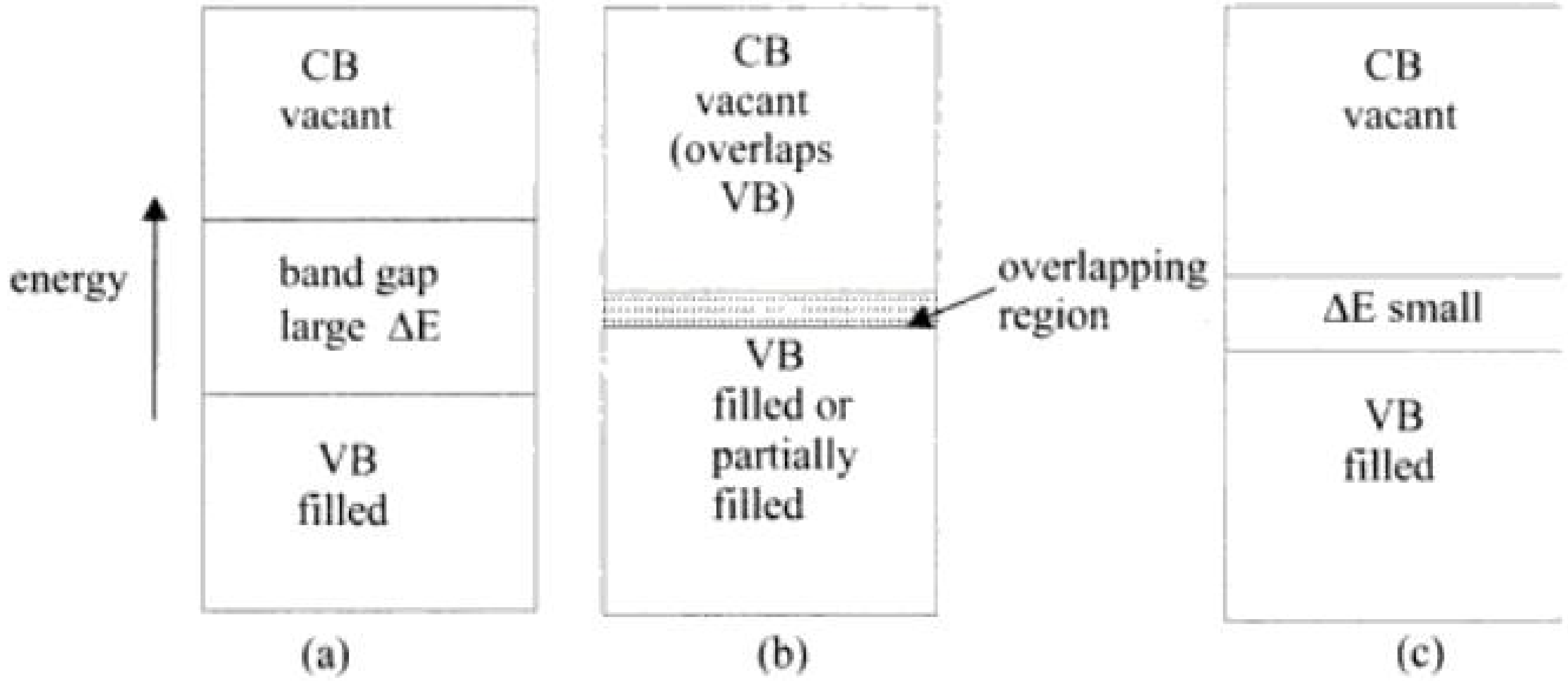


Fig. 3.26 Band structures of solids (a) insulators (b) conductors and (c) semiconductors

Insulators are those solids in which the valence band is completely filled with electrons and the conduction band is completely vacant with a large band gap separating the valence band from the conduction band. The band gap is of the order of several electron volts (eV) and electrons cannot be easily promoted from the valence band to the conduction band. Hence they are poor conductors of electricity. For example the covalent crystalline solid diamond has a band gap energy of 7 eV while the amorphous glass has a band gap energy of 10 eV and hence both these solids are good insulators. In general greater the band gap energy, better is the insulating capability. The electrical conductivity of insulators increases with increasing temperature as electrons acquire thermal energy and the probability of their promotion to the conduction band increases.

Conductors have partially filled or completely filled valence band and the vacant conduction band overlaps with the valence band and hence a band gap does not exist. Electrons can be easily promoted

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Paramagnetism of substances is attributed to the presence of unpaired electrons in the atoms, ions or molecules. A paramagnetic substance is attracted by an external magnetic field with a force proportional to the applied field strength times the field gradient. The magnitude of magnetic susceptibility is of several orders greater than that of diamagnetic substances lying in the range of 10^{-6} to 10^{-2} in cgs units. Paramagnetism varies inversely with temperature as shown in the Figure 3.28.

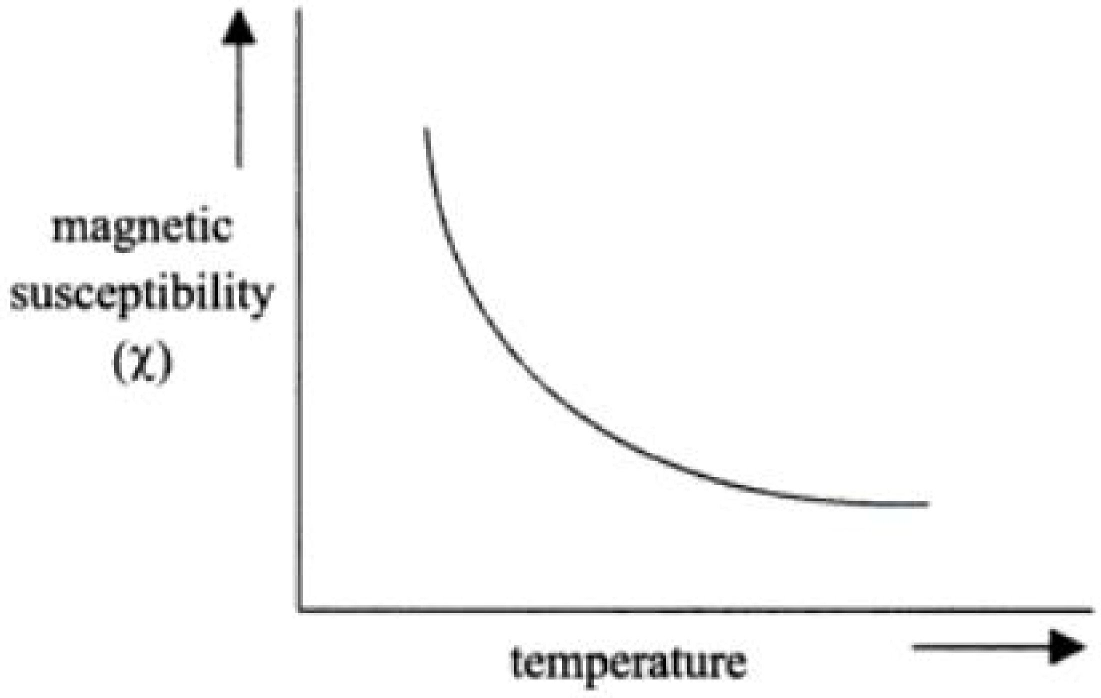


Fig. 3.28 Temperature dependence of magnetic susceptibility in a paramagnetic substance

Ferromagnetism and Antiferromagnetism depends on the interaction between the electron spins on many atoms and arises from the cooperative behaviour of many unit cells in a crystal. In a ferromagnetic substance the spins on different atomic centers are coupled into a parallel alignment as shown in the Figure 3.29 a.

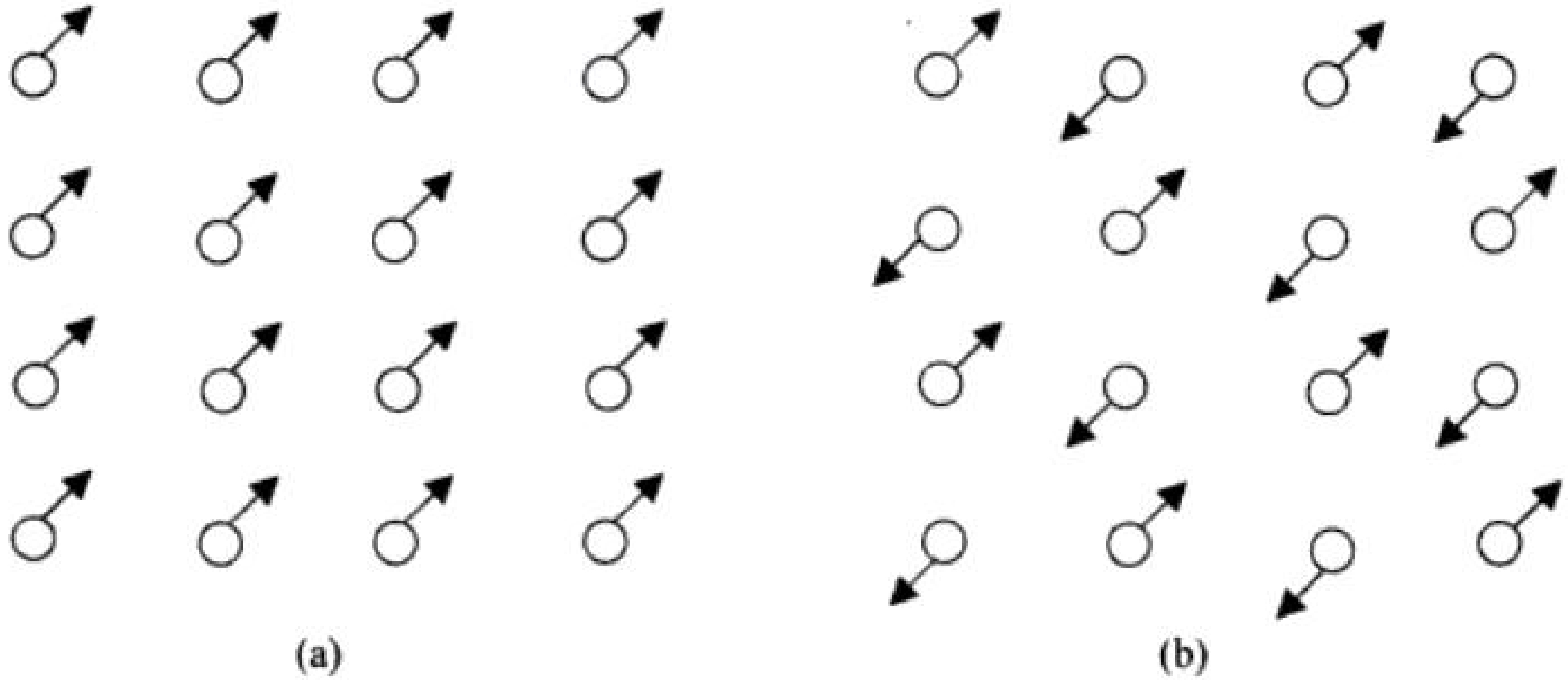


Fig. 3.29 Alignment of individual magnetic moments in (a) parallel in ferromagnetic materials and (b) antiparallel in antiferromagnetic materials

The cooperative behaviour is sustained over thousands of atoms in a *magnetic domain.*

The net magnetic susceptibility is quite large (10^{-2} to 10^{6}) as the individual magnetic moments of spins augment each other. Once the domain is established and the temperature maintained below a certain critical temperature called *Curie Temperature* (T_C) magnetisation persists because the spins are locked together. The effect of temperature on the magnetic susceptibility in ferromagnetic and antiferromagnetic substances is shown in the Figures 3.30 a and b. Ferromagnetism is exhibited by materials containing unpaired electrons in the d or f orbitals that couple with unpaired electrons in similar orbitals on the surrounding atoms. Ferrites with a stoichiometric formula of AFe_2O_4 (e.g., $ZnFe_2O_4$) having an inverted spinel structure exhibit both ferromagnetic (when $kT > J$) and antiferromagnetic behaviour (when $kT < J$) where J is the interaction energy of the spins on different ions.

(< 2%) distributed uniformly in the form of fibres. The carbon content is less than 0.15%. This purest form of iron is malleable, ductile, tough and has good corrosion resistance. It can be extruded, forged and hammer welded and can be case-hardened. Wrought iron is mostly used for manufacturing steel and for making products such as water pipes, corrugated sheets, wires, chains, hooks, nails, anchors, bolts and cores of electromagnets.

Cast iron contains carbon to the extent of 3-4% with smaller amounts of silicon, phosphorus, sulphur and manganese and is produced in a cupola furnace. Different forms of cast iron include grey cast iron, white cast iron and malleable cast iron. *Grey cast iron* (grey coloured mixture of ferrite and graphite) with most of the carbon present as flakes of graphite is produced when the silicon content is relatively high (2-2.5%) and the molten metal is cooled slowly. Grey cast iron is soft and fusible but less tough and less ductile. It has high compressive strength but a low tensile strength. It can be machined and cast into in moulds of required shapes. Cast iron is used for making castings, dies, moulds, bodies, beds and bases of machinery, pistons and cylinders for automobiles etc. *White cast iron* is produced when the silicon content is less than 1% and the molten metal is cooled rapidly. Carbon (~ 3%) exists mostly in the combined form of cementite which renders the metal hard, brittle and wear resistant. Hence the metal cannot be machined by ordinary tools. It does not easily rust. White cast iron finds use only where wear resistance is required such as in railway carriage brakes. It is mostly converted to malleable cast iron. *Malleable cast iron* is produced by the heat treatment of white cast iron. The white cast iron is heated to about 875° C, maintained at this temperature for about 24 hours followed by annealing to room temperature. The cementite in the white cast iron dissociates and carbon deposits in the form of nodules. Malleable cast iron is ductile, tough, with good shock resistance and machinability combining the advantageous properties of both grey and white cast irons. However it cannot be drawn into wires or hammered into sheets. Malleable cast iron is used for making agricultural machinery, toothed wheels, screw propellers, automobile parts such as pedals, hubs, gear and rear-axle housings, carpentry tools etc.

3.19 Alloys

Most of the pure metals have good physical and mechanical properties such as ductility, malleability, lustre, electrical and thermal conductivities etc. but are soft, chemically reactive and susceptible for corrosion. The physical and mechanical properties of metals are modified to a large extent making metals more suitable for engineering applications by alloying them with metals and even non-metals. Alloying may be carried out with specific aims, such as to increase hardness and tensile strength, enhance corrosion resistance, improve better casting characteristics or to lower the melting temperature.

Binary alloys are mostly prepared by any of the three methods (i) fusion (ii) electrodeposition and (iii) chemical reduction. *Fusion* of two metals is usually carried in refractory lined crucibles by melting the higher melting metal first to which the second metal with the lower melting point is added. The molten mass is stirred thoroughly to ensure proper mixing and achieve uniform composition. *Electrodeposition* of two metals simultaneously from an electrolytic bath containing the salts of the metals is yet another method. For example, brass is prepared by the simultaneous deposition of copper and zinc from a bath containing cyanides of the two metals. *Reduction* of a compound of one metal in the presence of a second metal is also practiced as in the case of copper- aluminium alloy (aluminium bronze) by reducing alumina (Al_2O_3) in the presence of copper.

Steel, an alloy of iron and carbon, occupies a prime position in industrial as well as constructional activities. The quantum of production and usage of steel serves as an index of the economic strength of a nation.

3.20 Shaping of Metals and Alloys

Metals and alloys are made available commercially in the form of semi-finished products such as slabs, plates, rods, pipes, foils, powders, filings, wool and wires. A variety of methods are used for shaping the metals and alloys including (i) casting (ii) extrusion (iii) roller milling and (iv) powder metallurgy.

3.20.1 Casting

Casting methods include mould casting, die casting, centrifugal casting, investment casting and slush casting.

Mould Casting involves making a clay or plaster of Paris based green sand mould which is a replica of the object. The green sand mould is baked to a dry sand mould and the mould is covered with a 'core' to form hollow or cylindrical shaped objects, a 'gate' to introduce the molten metal into the mould and 'riser' to allow the air to escape from the mould as the molten metal is poured. Precision objects of identical shapes can be mass produced by mould casting.

Die Casting is carried out in a permanent mould of harder materials than the cast material and pressure is applied on the melt to take the shape of the mould. Automobile parts, valves, surgical instruments are made by die casting

Centrifugal Casting is especially suitable for making cylindrical objects such as pipes, tubes etc, in which the molten metal is poured into a fast-rotating permanent mould. The metal clings to the walls of the mould by centrifugal force leaving the centre hollow. On cooling the cylindrical shaped object is formed.

Investment Casting involves making a wax cast of the object which is embedded (invested) in a fluid ceramic material and the ceramic mould is allowed to solidify. The ceramic mould is heated to melt the wax which flows out leaving a cavity of the desired shape in the ceramic mould. Molten metals are poured into the ceramic mould and after the molten metal solidifies the ceramic mould is broken to get the finished metal object.

Slush Casting is used to make hollow castings. A low melting alloy or metal is poured into a bronze or plaster mould and the excess molten alloy or metal is quickly poured out after a thin solid shell is formed. The casting is then finished by electroplating or lacquering.

3.20.2 Roller milling

Roller milling is adopted for making thin films and sheets. Rectangular blocks of metals and alloys are heated and passed through rollers until the big block is brought down to the suitable size and then cold-rolling is continued to make the desired sheets or films.

3.20.3 Extrusion

Extrusion is used to make tubes, pipes, wires, lead-covered telephone cables, etc. Metals and alloys are heated to red-heat (~700–800° C) and forced through a die in the extrusion press.

3.20.4 Powder metallurgy

Powder metallurgy has become one of the most sophisticated and viable methodology for shaping a wide range of objects from metals, alloys, ceramics and composites. Most metals and alloys cannot

4 ELECTROCHEMISTRY

4.1 Introduction

Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy into chemical energy and vice versa. Electrolysis, electrometallurgy, electroplating, etc. use electrical energy to drive chemical reactions, while chemical energy is transformed into electricity in galvanic cells, batteries and fuel cells. Substances such as metals and alloys conduct electricity under the influence of an applied electric potential through a flow of electrons and hence are known as *electronic conductors*. The flow of electricity in electronic conductors does not cause any physical or chemical change in the conductor. On the other hand electrolyte solutions and molten salts conduct electricity through the migration of ions and are known as *electrolytic conductors* or *electrolytes*. When direct current is passed through an electrolyte solution; decomposition and changes occur in the composition of the electrolyte.

4.2 Electrolysis

Electrolysis involves the use of electricity from an external source for performing chemical reactions. Electrolysis requires the use of electrolytic conductors (electrolyte) as well as electronic conductors (electrodes) which are the essential components of an electrolytic cell. Chemical reactions always occur at the electrodes and may be explained in terms of the oxidation and reduction reactions. One of the electrodes, called the anode, is connected to the positive terminal of a d.c. source of electricity while the second electrode called the cathode is connected to the negative terminal of the battery.

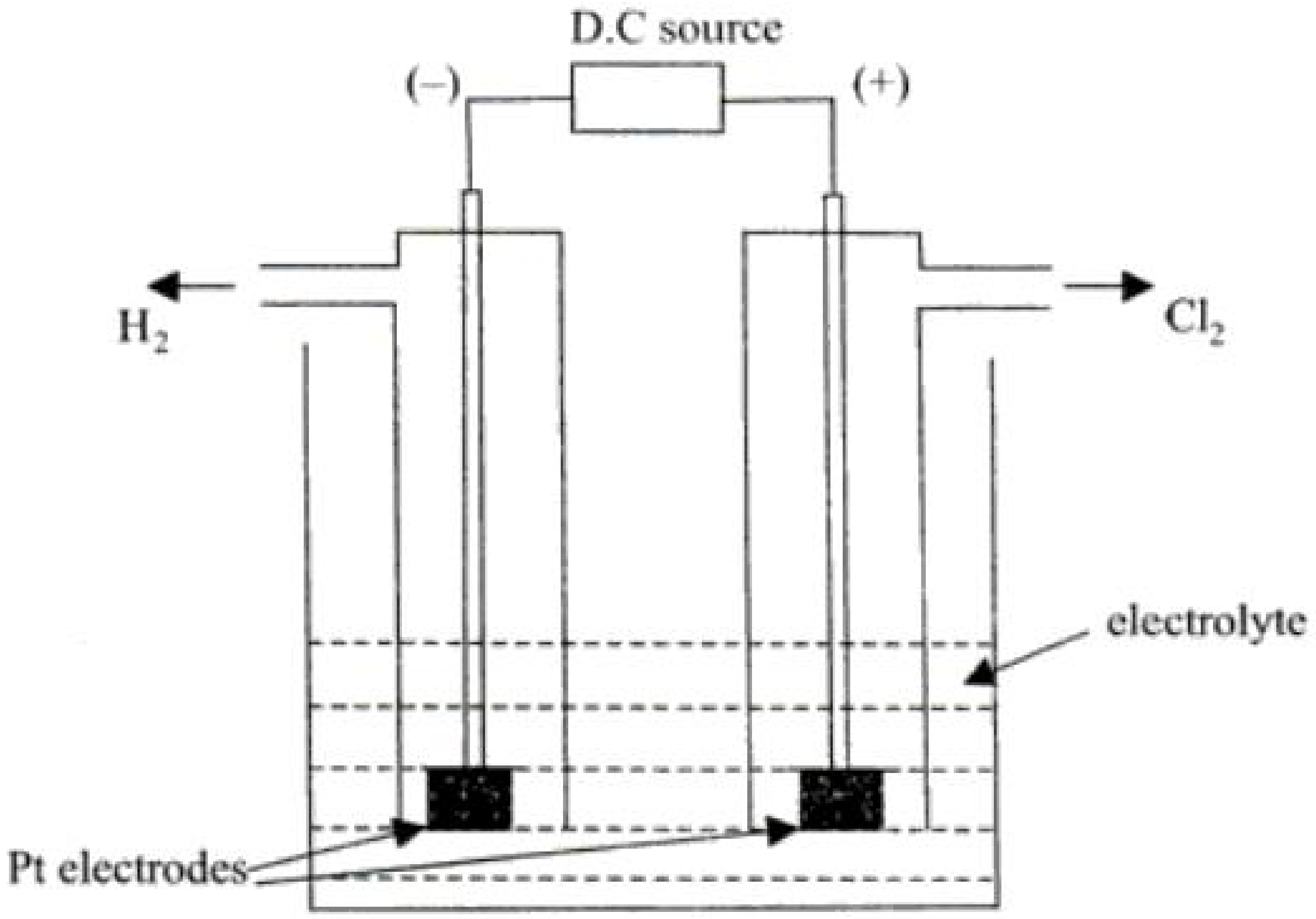
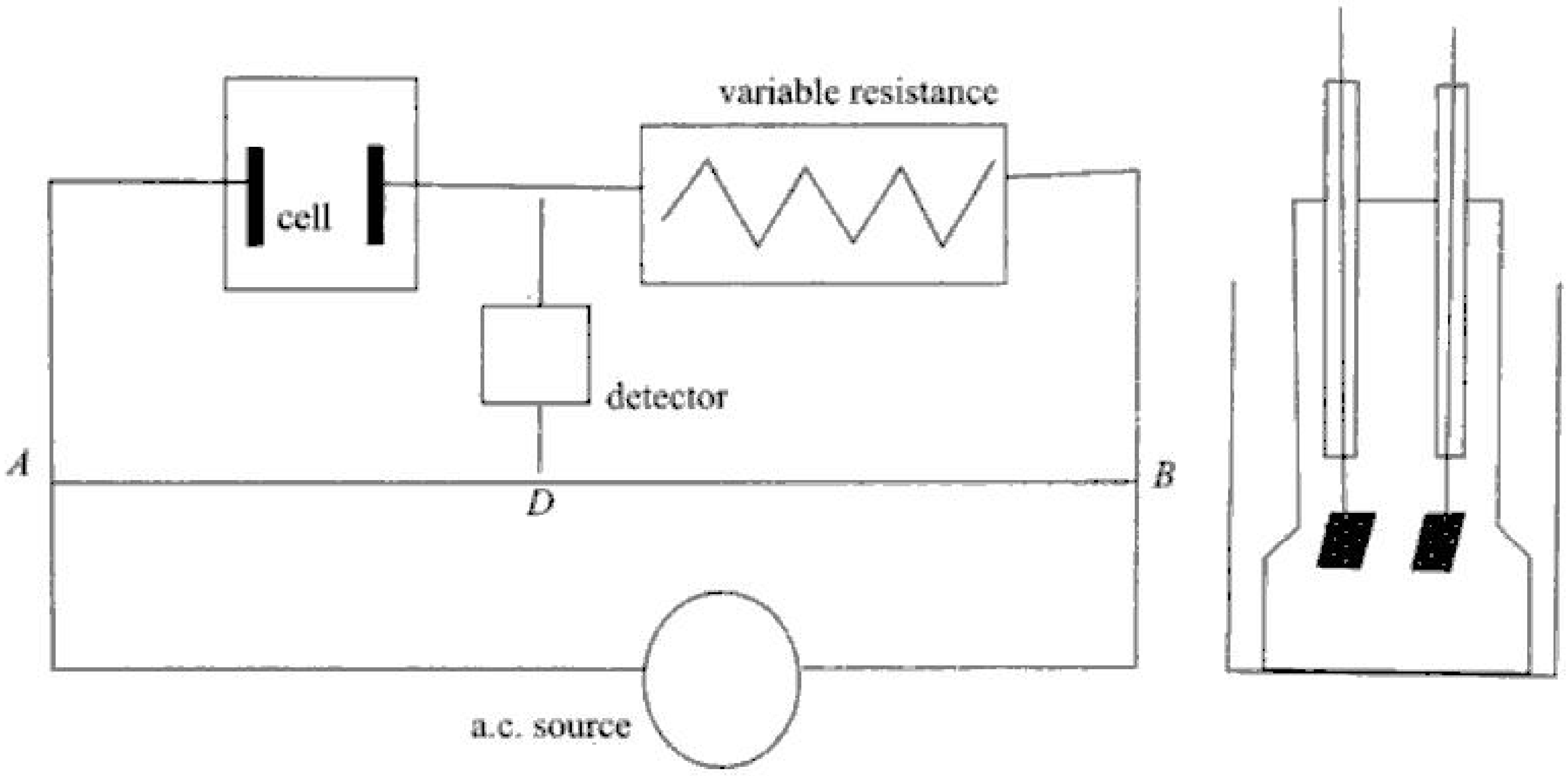


Fig. 4.1 Schematic diagram of an electrolytic cell

4.5.1 Measurement of conductance

Conductometry involves the measurement of an electrolytic conductance under relatively mild conditions of low voltage of about 1–100 V, and frequencies of alternating current of less than 5000 Hz. In electrolyte solutions the magnitude of current flowing in the circuit depends on the number and types of ions present in the electrolyte solution, their mobility, the nature of the solvent and the voltage applied. In a given dilute electrolyte solution of strong electrolytes the number of ions depends on the concentration while in solutions of weak electrolytes it is also dependent on the degree of dissociation or ionisation and on the temperature. Hence measurement of conductance provides information on the concentration of electrolyte solutions.

The instrumentation required for the measurement of conductance is quite simple and inexpensive. Conductometry finds extensive use in the industry both as an analytical tool and also in process control. The conductance meter or bridge for measuring conductance of a solution is based on a Wheatstone bridge circuit (Figure. 4.2).



(a) wheatstone bridge circuit (b) conductance cell

Fig. 4.2 Measurement of conductance

The resistance of the electrolyte solution R_C placed in a conductance cell consisting of platinised Pt electrodes is measured using alternating current to prevent any deposition on the electrodes during electrolysis. The platinum black of the platinised electrodes adsorbs gases of hydrogen and oxygen formed by the successive pulses of alternating current and catalyses their combination. A signal generator such as a variable frequency oscillator, a null detector-indicator such as ear phones or a sensitive micro ammeter is used as a detector. The point D along the slide wire AB at which no current flows in the circuit is detected and the resistance of the cell is calculated using the formula

$$R_C/R_K = AD/DB \tag{4.14}$$

Where R_K is the known resistance (that of standard KCl solution). The specific conductance of the electrolyte is calculated using the Eq. 4.13 once the cell constant is known.

A variety of conductance cells are available commercially. The most widely used type has a pair of platinised platinum electrodes of about 1 cm^2 area welded to a platinum wire and sealed rigidly in a

$cm^2\ V^{-1}\ s^{-1}$. Ionic mobility at infinite dilution (u_0) is related to ion conductance at infinite dilution λ_0 and is given as

$$\lambda_0 = u_0 F \tag{4.21}$$

The equivalent conductance at infinite dilution Λ_0, ionic mobilities of the constituent cation and anion of the electrolyte and transport number are related by equations

$$\Lambda_0 = F\,[(u_0)_c + (u_0)_a] \tag{4.22}$$

$$\frac{(\lambda_0)_c}{\Lambda_0} = \frac{u_c}{(u_c + u_a)} = (t_0)_c \tag{4.23}$$

A similar equation relating the transport number and ionic conductance may be written for the anion also.

4.7 Theories of Acids and Bases

Arrhenius defined acids as compounds that give hydrogen ions (H^+) in aqueous solution while bases as those which give hydroxyl ions (OH^-) in aqueous solution. Accordingly acids such as hydrochloric, nitric and sulphuric acids ionise readily and give hydrogen ions and hence are considered as strong acids. In contrast acetic acid, oxalic acid, etc ionise feebly and yield only very low concentration of hydrogen ions and are hence classified as weak acids. Similarly, strong bases are those that ionise readily to give hydroxyl ions (e.g., sodium hydroxide, potassium hydroxide etc.) while calcium hydroxide and magnesium hydroxide are classified as weak bases. The definition was applicable only to aqueous solutions. It was found that in non-aqueous liquid ammonia as a solvent ammonium chloride behaves as an acid and sodamide behaves as a base. Similarly, in liquid sulphur dioxide thionyl chloride behaves as an acid and ammonium sulphite behaves as a base. Another disadvantage with Arrhenius definition is that bases are considered to contain OH groups whereas organic compounds such as pyridine, aliphatic amines, etc. behave as bases in aqueous solution even though they do not contain the OH group.

Bronsted and Lowry independently put forward the *proton transfer theory* and defined an acid as a proton donor, that is, a substance with a tendency to lose a proton while a base is a proton acceptor with a tendency to accept protons. The acid-base relationship may be shown as

$$\underset{\text{acid}}{A} \rightleftarrows \underset{\text{base}}{B^-} + \underset{\text{proton}}{H^+} \tag{4.24}$$

The remaining portion of the acid after it loses a proton (B^-) exhibits a tendency to regain the proton and hence is called the *conjugate base* of the acid A and A is the *conjugate acid* of the base B^-. The conjugate acid-base pair differs by a proton. Examples of conjugate acid-base pair include HCl and Cl^-; NH_4^+ and NH_3; H_2O and OH^-.

In aqueous solutions the proton exists as a hydrated (solvated) hydronium ion (H_3O^+) and the solvent water itself may be considered as a base accepting a proton.

$$\underset{\text{acid 1}}{HCl} + \underset{\substack{\text{base 2}\\\text{(solvent)}}}{H_2O} \rightleftarrows \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{Cl^-} \tag{4.25}$$

The interaction between acid 1 and base 2 results in the formation of another conjugate acid (H_3O^+) to the base 2 (H_2O) and also another conjugate base (Cl^-) to the acid 1(HCl).

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A typical example of a basic buffer is the mixture of ammonia (ammonium hydroxide) and ammonium chloride. Ammonia is weakly ionised while ammonium chloride is completely ionised.

$$\begin{array}{c} \text{BOH} \qquad\qquad \text{B}^+ \\ NH_4OH \rightleftharpoons NH_4^+ + OH^- \end{array} \tag{4.44}$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \tag{4.45}$$

The ionisation of ammonium hydroxide is suppressed by the common ion (NH_4^+) in the completely ionised salt. When a small amount of acid is added to this buffer the buffer action takes place by the added H^+ reacting with the base to form water and the ammonium ion.

$$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O \tag{4.46}$$

When a small amount of a base is added to the buffer the added OH^- from the base combines with NH_4^+ to form more of unionised ammonium hydroxide thereby resisting the change in pH.

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \tag{4.47}$$

The pH of buffers may be calculated as follows. In an acidic buffer of the type $HA–A^-$ all the A^- may be assumed to come from the completely ionised salt with the dissociation of HA being negligible. The concentration of the A^- in the buffer may be taken as equal to the molar concentration of the salt itself. The dissociation of the weak acid in the presence of A^- will be suppressed to a large extent and the concentration of the acid taken used for the preparation of the buffer itself may be taken as the concentration of unionised HA. The dissociation and the acid dissociation constant K_a of the weak acid may be represented as

$$HA = H^+ + A^- \; ; K_a = [H^+][A^-]/[HA] \tag{4.48}$$

Therefore

$$[H^+] = K_a([HA]/[A^-] \text{ or } K_a\,(C_a/C_s) \tag{4.49}$$

Where C_a represents the concentration of the unionised acid (almost equal to the original concentration of the acid) and C_s is the molar concentration of the salt. Taking logarithms and changing the sign

$$-\log [H^+] = -\log K_a - \log (C_a/C_s) \tag{4.50}$$

or

$$pH = pK_a + \log (C_s/C_a) = pK_a + \log \{[salt]/[acid]\} \tag{4.51}$$

The above equation is known as the *Henderson-Hasselbach equation.* Since the concentrations are known as also the value of pK_a for the given weak acid it is possible to substitute the values to calculate the pH.

In the case of a basic buffer of the type $BOH–B^+$ type the ionisation of the weak base is suppressed and all the B^+ in the buffer is from the completely ionised salt and the hence equal to the molar concentration of the salt itself. Similarly the concentration of base itself may be taken as the concentration of the unionised BOH in the buffer. The dissociation of the weak base and its dissociation constant K_b may be represented

$$BOH = B^+ + OH^- \; ; \; K_b = ([B^+]\,[OH^-]/[BOH]\,) \tag{4.52}$$

Therefore

$$[OH^-] = K_b\{[BOH]/[B^+]\, K_b\,(C_b/C_s) \tag{4.53}$$

Where C_b represents the concentration of the unionised base (almost equal to the original concentration of the base) and C_s is the molar concentration of the salt. Taking logarithms and changing the sign

$$-\log [OH^-] = -\log K_b - \log (C_b/C_s) \tag{4.54}$$

or

$$pOH = pK_b + \log (C_s/C_b) = pK_b + \log \{[salt]/[base]\} \tag{4.55}$$

$$pH = 14 - pK_b - \log \{[salt]/[base]\} \tag{4.56}$$

When a cell is connected in series with a galvanometer and the circuit is closed, the galvanometer shows a deflection indicating that a current is flowing through the circuit. The flow of current from one electrode to another is due to the potential difference between the two electrodes. The potential difference which causes a current to flow from the electrode of higher potential to the one of lower is called the *electromotive force* (emf) of the cell and is expressed in volts. The voltage of the cell can be measured by a voltmeter connected across the two electrodes. The measured voltage will depend on the current drawn by the voltmeter and the sum of the resistances of the external circuit and the internal resistance of the cell. The emf of the cell is the maximum voltage of the cell that can be measured when zero current is drawn during measurement. A *potentiometer* can be used to measure the emf of the cell under conditions of zero current flow.

4.10 EMF Measurement

The emf of any electrochemical cell (x) is measured conveniently by the Poggendorf compensation method using a potentiometer (Figure. 4.6). The potentiometer consists of a platinum wire *AB* connected to a dc source (2–4 volts). The emf of the cell (x) is measured by comparing with the emf of a standard Weston cadmium cell (S.C.) whose emf is accurately known and remains constant at a given temperature. The emf of the Weston cadmium cell at 20° C is 1.01864 V and the temperature coefficient of the emf is negligible (about 4×10^{-5} V/deg). The positive terminal of the Weston cell is connected to the end A of the potentiometer wire and the negative terminal is connected through a galvanometer (G) to the sliding contact on the wire *AB*. The potentiometer is calibrated by including the S.C. in the circuit by the double pole-double throw (DPDT) switch and closing the key. The sliding contact is moved along the wire AB till there is no deflection (zero current flow) in the galvanometer (point C on the wire). The emf of the standard cell (E_{SC}) is proportional to the length *AC* as the potential drop across *AC* is exactly balanced by the E_{SC}. The electrochemical cell (x) whose emf is to be determined is now included in the circuit and the sliding contact moved along the wire AB to determine the position D when the galvanometer shows null deflection. The potential drop across AD is proportional to the emf of the unknown cell. The emf of the unknown cell E_X is calculated by the formula

$$E_X = (AD / AC)\, E_{SC} \tag{4.67}$$

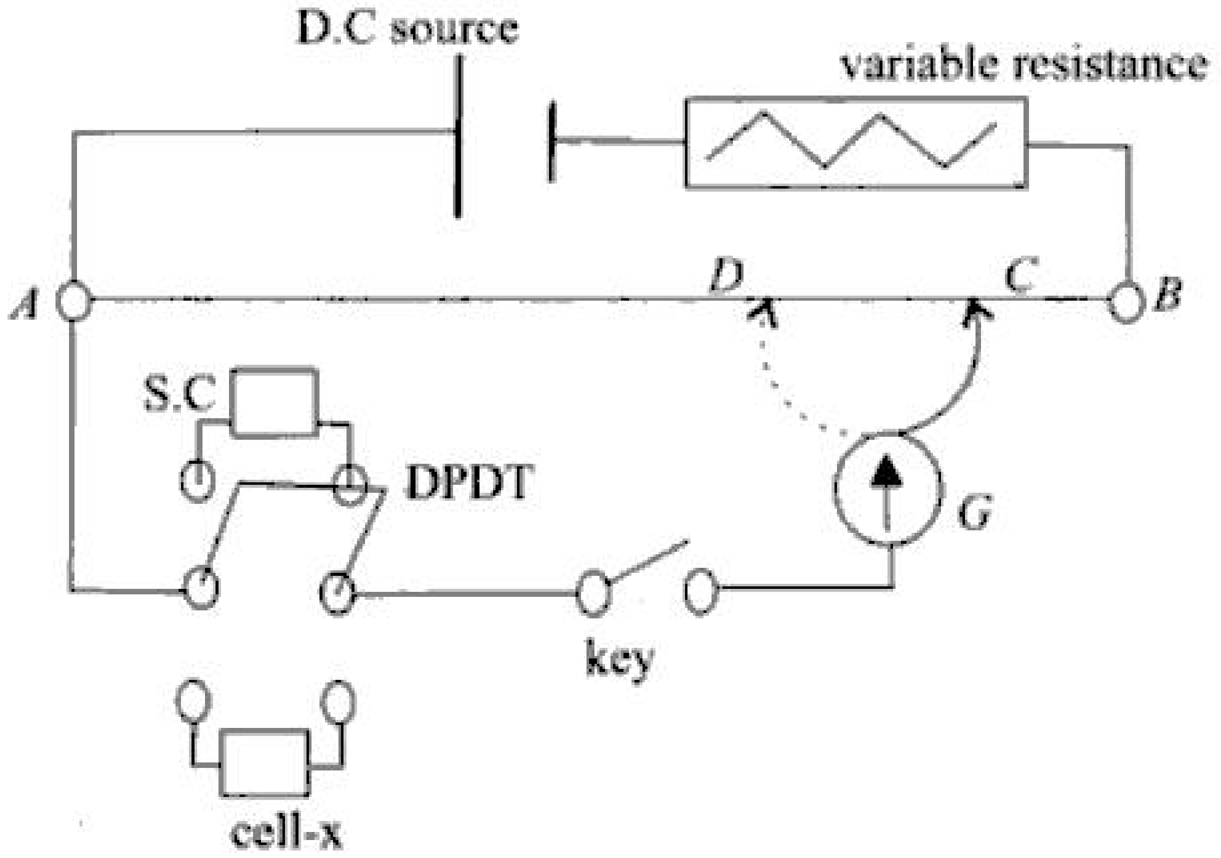

Fig. 4.6 Measurement of emf by Poggendorf's compensation method

Gas electrodes consist of a gas bubbling about an inert metal wire or foil immersed in a solution containing ions to which the gas is reversible. Thus hydrogen electrode consists of a platinum wire/foil coated with platinum black dipping in a solution of H^+ ions through which hydrogen gas is bubbled. The platinum wire/foil facilitates the establishment of equilibrium between the hydrogen gas and H^+ ions and also provides the electrical contact for the electrode. The hydrogen electrode is represented as Pt $|H_2|$ H^+ and the electrode reaction as

$$\tfrac{1}{2} H_2 (g, Pt) \rightleftarrows H^+(aq) + e^- \tag{4.87}$$

The electrode potential is determined both by the activity of hydrogen ions and the pressure of hydrogen gas as given by

$$E = E^\circ - 0.059 \log ([H^+]/[H_2]^{1/2}) \tag{4.88}$$

Since the activity of hydrogen gas in its normal sate of existence is unity, the potential of the hydrogen electrode when $[H^+] = 1$ is related to pH as $E = -0.059$ pH.

Oxidation-reduction electrodes consist of an inert contact or electronic conductor such as a platinum wire in contact with a solution containing a substance in two different oxidation states. For example, Pt | Fe^{3+}, Fe^{2+} is a typical oxidation-reduction electrode where the reaction taking place is

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \tag{4.89}$$

The electrode potential depends on the ratio of the activities of the two ions as

$$E = E^\circ - 0.059 \log ([Fe^{2+}]/[Fe^{3+}]) \tag{4.90}$$

4.13 Measurement of Single Electrode Potentials

The absolute potential of the half-cell or a single electrode can be determined by constructing an electrochemical cell in combination with another single electrode such that the electrochemical reaction is the sum of the two electrode reactions, one of which is oxidation and the other a reduction. The emf of the electrochemical cell is the algebraic sum of the two single electrode potentials constituting the cell.

$$E_{\text{cell}} = E_1 + E_2 \tag{4.91}$$

Where E_1 and E_2 are the potentials of the two single electrodes. Only the potential difference can be measured experimentally. Hence the potential E_1 can be determined from the experimentally determined value of E_{cell} (using Poggendorf method) only if the value of E_2 is known. Electrodes whose potentials are exactly known and can be used for constructing the electrochemical for the determination of single electrode potentials are called *reference electrodes*.

4.13.1 Reference electrodes

Reference electrodes are electrodes at which the oxidation or reduction reaction occurs reversibly. A single electrode is considered as a reference electrodes when it satisfies certain conditions. The electrode potential should remain constant for a long time with a negligible temperature coefficient, that is, the variation of potential with temperature should be negligible. Reference electrodes used in electrochemistry include the standard hydrogen electrode, calomel electrode and the silver-silver chloride electrode.

Standard hydrogen electrode (SHE)

The SHE consists of a piece of platinised platinum foil sealed inside a glass tube and surrounded by hydrogen gas at 1 atm. pressure and immersed in a solution containing hydrogen ions of unit activity. The potential of the SHE is *arbitrarily fixed as zero volt* at all temperatures as suggested by Nernst. Figure. 4.8 shows a diagrammatic sketch of the SHE. The electrode reaction is represented by the Eq. 4.87.

in the internal electrolyte and the sample solution. Any change in the gas concentration in the internal electrolyte brings about a change in pH which is sensed by the glass electrode/reference electrode pair. For example the CO_2 gas sensing electrode has a sodium hydrogen carbonate solution as the internal electrolyte and the cell reaction may be represented as

$$CO_2\,(\text{sample}) + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-\,(\text{internal electrolyte}) \qquad (4.109)$$

The concentration of bicarbonate ions in the internal electrolyte is considered as constant as its concentration is large compared to other species. The pH response of the glass electrode/reference electrode pair is a function of dissolved carbon dioxide in the sample solution.

4.17.4 Potentiometric titrations

The detection of the end point of a volumetric titration by the use of potentiometer is an important application of measurement of emf. The emf of the cell consisting of an indicator electrode responsive to the analyte ions and a reference electrode is measured as a function of the volume of titrant added to the analyte solution. Such potentiometric titrations are useful in quantitative analysis involving acid-base, red-ox and precipitation reactions and have been discussed in detail in Chapter 10 Sec. 10.6.2

4.17.5 Determination of solubility of sparingly soluble salts from emf measurements

The solubility product K_{sp} of a sparingly soluble salt is an equilibrium constant and is related to the emf of the cell in which the reaction such as

$$AgBr(s) \rightleftharpoons Ag^+ + Br^- \qquad (4.110)$$

occurs in a saturated solution of the salt. It is possible to construct a cell by coupling two single electrodes whose reactions lead to the over-all reaction given above. The solubility product of the sparingly soluble salt may be calculated from the emf of the cell and the known emf of the single electrodes. Thus in a cell consisting of a combination of silver and silver-silver bromide electrodes the electrode reactions at the two electrodes will be respectively

$$Ag(s) \rightleftharpoons Ag^+ + e^- \qquad (4.111\ a)$$

and

$$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^- \qquad (4.111\ b)$$

And the overall cell reaction will be the sum at the two electrodes and the same as in the Eq. 4.110. The E^0 values of the silver and the silver-silver bromide electrodes are -0.7991 and $+0.0711$ V respectively at 25° C and hence E^0 for the cell is the algebraic sum and equal to -0.7280 V. Substituting the calculated value of E^0 into

$$E^0 = 0.0591 \log K_{sp} \qquad (4.112)$$

the value of K_{sp} can be calculated as 4.9×10^{-13}.

Alternatively the solubility and solubility product constant of sparingly soluble salts such as silver chloride, lead sulphate etc., can be determined by measuring the emf of the single electrode reversible to one of the ions of the sparingly soluble salt and immersed in a saturated solution of the salt. For example the potential of the Ag-AgCl electrode in contact with a potassium chloride solution of chloride ion activity of a_{cl}^- depends also on a_{AG}^+ as given by

$$E = E^0 - 0.059 \log Ag^+ \text{ at } 25°C \qquad (4.113)$$

If the Ag | AgCl | KCl system is coupled with the SCE and the emf of the cell is measured it is possible to calculate the a_{ag}^+ from the known E^0 value for the Ag |Ag$^+$ electrode. Since the activities of both Ag$^+$ and Cl$^-$ are known K_{sp} can be calculated as $K_{sp} = (a_{ag}^+ . a_{Cl}^-)$.

Overvoltage is commercially exploited in the Castner-Kellner cell for the electrolysis of sodium chloride to produce sodium hydroxide and chlorine gas. Electrodeposition of sodium can occur even from an aqueous solution of sodium chloride on a mercury cathode. This is possible because the discharge potential of sodium is only –1.2 V on a mercury cathode while the discharge potential for hydrogen is –1.4 V. Sodium gets deposited on the mercury cathode forming an amalgam. However when the amalgam is treated with water in an iron vessel, the discharge potentials change for the cell Fe | Na–Hg–H_2O | Fe. The discharge potentials for hydrogen and sodium are < 0.2 V and –2.7 V respectively. This results in the discharge of H^+ ion at the cathode and evolution of hydrogen while sodium dissolves in water containing excess of hydroxide ions forming sodium hydroxide. Chlorine is evolved at the anode instead of oxygen because the discharge potential for chlorine is +1.31 V compared to that of oxygen of +1.41 V under the operating conditions of the electrolytic process.

4.20 Electrochemical and Electrometallurgical Applications

The applications of electrochemistry in electrochemical and electrometallurgical industries are quite large and include major industries such as chlor-alkali, inorganic and organic electrosynthesis and extraction, refining and production of metals. In addition electrochemical technology also finds extensive applications in water purification, effluent treatment, recycling of materials, metal and material processing and finishing, corrosion and its control, batteries and fuel cells and electrochemical sensors and monitoring techniques. This section deals with a few important applications in electrochemical technology and electrometallurgy.

4.20.1 Chlor-alkali industry

The term chlor-alkali refers to one of the largest electrochemical industries for the production of sodium hydroxide (caustic soda) and gases of chlorine and hydrogen with a worldwide production of more than 50 million tons per annum. Aqueous sodium chloride (brine) obtained from natural salt deposits is electrolysed yielding sodium hydroxide (normally traded as lye, a 50% aqueous solution) and chlorine gas as the main products of commercial importance and hydrogen which is mostly used as a fuel in the power plant associated with chlor-alkali industry. Chlorine is mostly consumed in the chemical industry complex for the manufacture of polyvinyl chloride, chlorinated hydrocarbons, propylene oxide and other chemicals while caustic soda has a wide range of uses in the manufacture of organic and inorganic chemicals, aluminum extraction, manufacture of textiles, rayon, paper, soap and detergents and oil refining.

Three different electrochemical technologies are currently in use, based on (i) mercury (ii) diaphragm and (iii) membrane cells, the third gradually replacing the first two older technologies. The electrode reactions that occur during the electrolysis of brine involves the oxidation of chloride to chlorine at the anode and the reduction of water directly to hydroxide ions at the cathode in the diaphragm and membrane cell technologies and may be represented as

$$2\,Cl^- - 2\,e^- \longrightarrow Cl_2 \qquad \text{(at the anode)} \qquad (4.114)$$

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + OH^- \qquad \text{(at the cathode)} \qquad (4.115)$$

the hydroxide ions interacting with Na^+ ions to form the caustic soda.

discharged at the cathode. The extraction of these metals may be described with the typical example of sodium production in the Down's process. The Down's cell (Figure. 4.14) consists of a steel tank lined with refractory bricks provided with a cylindrical graphite anode and a steel cathode surrounding the anode.

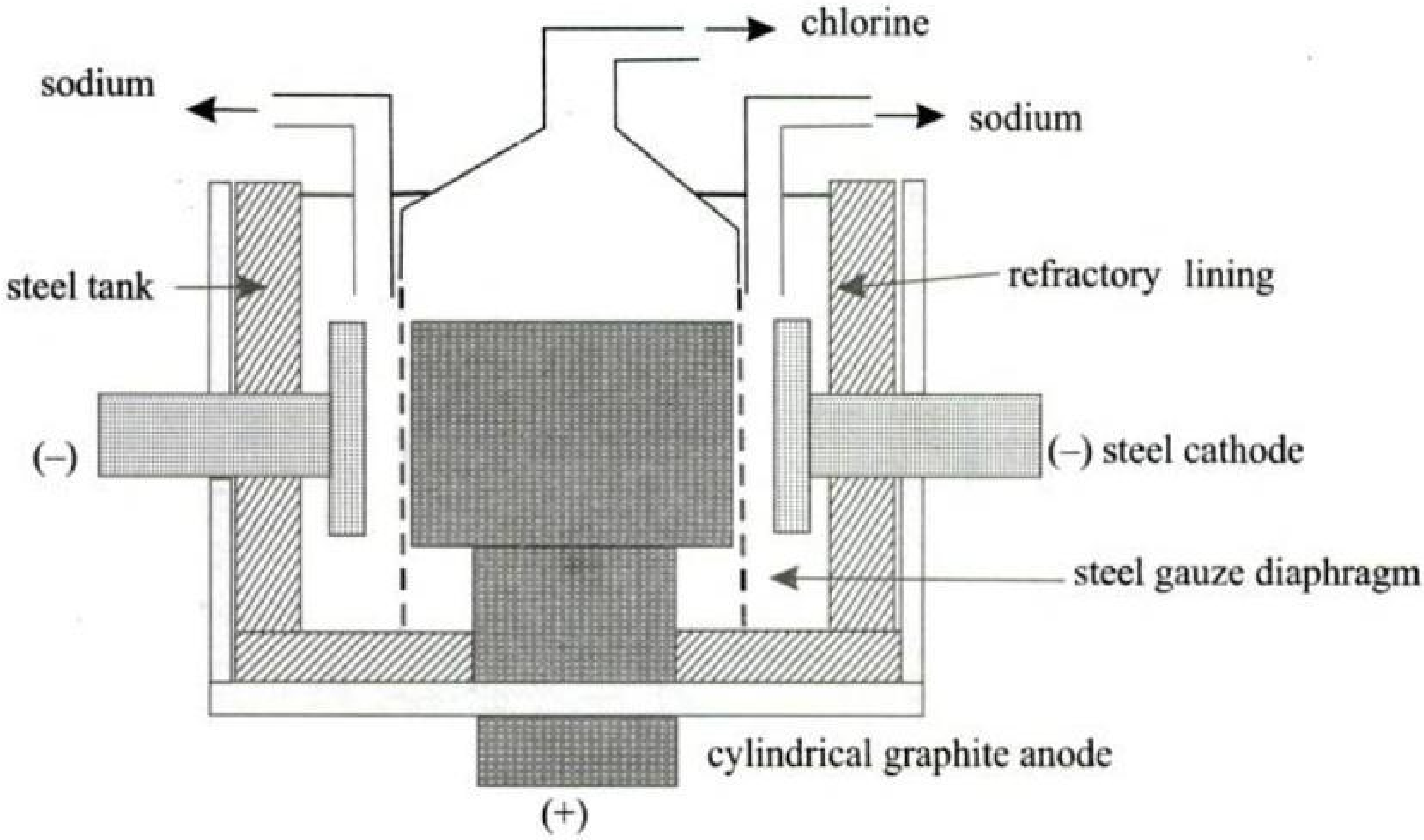

Fig. 4.14 Down's cell for extraction of sodium metal

The electrolyte is a molten mixture of sodium chloride (40%) and calcium chloride (60%) requiring a process temperature of about 600° C. The electrode reactions may be represented as

$$2\,\mathrm{Cl}^- - 2\,e^- \longrightarrow \mathrm{Cl}_2 \text{ (at the anode)} \tag{4.119}$$

and

$$\mathrm{Na}^+ + e^- \longrightarrow \mathrm{Na} \text{ (at the cathode)} \tag{4.120}$$

The products are separated to prevent the back reaction by a steel guaze diaphragm and the liquid sodium, being less dense readily rises up a pipe into the sodium reservoir. Calcium also formed at the cathode being more dense sinks back into the electrolyte to establish the equilibrium

$$\mathrm{Ca} + 2\,\mathrm{NaCl} \rightleftharpoons \mathrm{CaCl}_2 + 2\,\mathrm{Na} \tag{4.121}$$

Down's cell operates a about 1 A/cm^2 with a cell voltage of about –7 V.

4.20.4 Electrolytic refining

The objective of electrolytic refining is to purify the desired metal and remove unwanted elements (mostly metals). The impure metal is made the anode and the electrolytic process deposits the pure metal at the cathode, the other metals being left as an anode sludge or as anions in the electrolyte solution. Electrorefining process is adopted when highly pure metal is required (e.g. copper in electronic applications) as well as to assist in the recycling of metals and the separation of metals from complex mixtures found in scrap. The more important electrorefined metals include copper, tin, lead, nickel,

Table 4.4 Electroplating conditions and applications of a few metals

Metal	*Composition of plating bath (Metal conc. g/dm^3)*	*Current density (mA/ cm^2)*	*T (° C)*	*Additives*	*Anode*	*Applications*
Cu	CuCN (40–50) KCN (20–30) K_2CO_3 (10)	10–40	40–70	Na_2SO_3	O_2-free Cu	Undercoat
Ni	Ni sulphamate (600) $NiCl_2$ (5) H_3BO_3 (30) pH 4	50–400	50–60	Not essential	Ni pellets	Mirror finish
Ag	$KAG(CN)_2$ (40–60) KCN (80–100) K_2CO_3 (10)	3–10	20–30	S-contg. brightener	AG	Decorative finish
Zn	ZnO (6–10) NaOH(70–100)	10–30	20–40	Org. additives	Zn	Non-toxic coat
Cr	CrO_3(200) H_2SO_4 (2)	100–200	40–55	---	Pb-Sn / PbO_2	Hard wear-resistant coat

Typical applications of electroplating in the engineering industry include corrosion protection, restoration, decorative appeal, hardness, wear resistance, optical or thermal reflectivity, electrical conductivity, thermal conductivity, oil retention and solderability. Electroplating is extensively used in the electronic industry for lead-in conductors in large-scale integrated chips, printed circuit boards, electrical contacts and connectors, transistors, and switches.

Electroless plating involves an autocatalytic red-ox reaction, the oxidation of a soluble reducing agent R(to O) on some sites on the catalytically active substrate surface such that the overall process of deposition of metal occurs on the substrate.

$$M^{n+} + R \longrightarrow M + O \qquad (4.122)$$

The deposition of the metal occurs at a fast pace after being initiated by a nucleation process.

The electroless plating bath contains (i) a source of soluble electroactive metal (ii) a reducing agent (iii) a complexing agent (iv) an exaltant to increase the rate of plating (v) stabilizers to prevent bath decomposition (vi) additives and (vii) buffer to maintain pH. For example for electroless nickel plating the cell reactions may be represented as

$$Ni^{2+} + 2\,e^- \longrightarrow Ni;\ \text{(at the cathode)};\ E^0 = -\,0.25\ \text{V} \qquad (4.123)$$

$$\underset{\text{(hypophosphite)}}{H_2PO_2^-} + H_2O \longrightarrow H_2PO_3^- + 2\,H^+ + 2\,e^-\ \text{(at the anode)};\ E^0 = -\,0.50\ \text{V} \qquad (4.124)$$

The overall cell reaction being

$$Ni^{2+} + H_2PO_2^- + H_2O \longrightarrow Ni + H_2PO_3^- + 2\,H^+;\ \Delta G = -\,48.3\ \text{kJ/mol} \qquad (4.125)$$

The plating bath contains nickel chloride (30 g/dm^3), sodium hypophosphite (10 g/dm^3), ammonium citrate (65 g/dm^3) and ammonium chloride (50 g/dm^3) with the pH in the range 8–10 and temperature of 90° C.

The ammonia gas reacts with Zn^{2+} (in the electrolyte containing $ZnCl_2$) thereby preventing of the disruption of current flow.

$$Zn^{2+} + 2\,NH_3 + 2Cl^- \longrightarrow [Zn(NH_3)_2]Cl_2 \qquad (4.135)$$

The dry cell gives a voltage of about 1.5 V. The secondary reactions consume Zn^{2+} and OH^- ions and once the cell is discharged it cannot be recharged. The cell has two main disadvantages in that (i) zinc metal dissolves in the acidic electrolyte and hence the cell runs down even if it is not in use and (ii) when current is drawn rapidly, the voltage drops due to accumulation of products on the electrodes.

Other leclanche type cells

Heavy duty dry cell is a modified Leclanche cell with the same components but contains less of ammonium chloride and the electrolyte is mainly zinc chloride. The *Ruben-Mallory* dry cell consists of zinc anode, a paste of carbon and mercuric oxide (HgO-depolariser) as cathode and an electrolyte of 40% potassium hydroxide saturated with potassium zincate absorbed in cellulose or gelled with carboxymethylcellulose. The electrode reactions are

$$HgO + H_2O + 2\,e^- \longrightarrow Hg + 2\,OH^- \qquad \text{(at the cathode)} \qquad (4.136)$$

and

$$Zn + 2\,OH^- \longrightarrow Zn\,(OH)_2 + 2\,e^- \qquad \text{(at the anode)} \qquad (4.137)$$

The cell reaction may be represented as

$$Zn + HgO + H_2O \longrightarrow Zn(OH)_2 + Hg \qquad (4.138)$$

Magnesium-carbon leclanche type cell containing the more negative element magnesium ($E^\circ = -2.37$ V) as compared to zinc ($E^\circ = -0.76$ V) as anode, a carbon cathode and an electrolyte of gelled magnesium bromide containing lithium chromate to inhibit the corrosion of the anode generates a potential of 1.9 V. A mixture of MnO_2 and barium chromate is used as cathodic depolariser. The electrode reactions are

$$2\,MnO_2 + 2\,H_2O + 2\,e^- \longrightarrow 2\,MnO(OH) + 2\,OH^- \qquad \text{(at the cathode)} \qquad (4.139)$$

$$Mg + 2\,OH^- \longrightarrow Mg(OH)_2 + 2\,e^- \qquad \text{(at the anode)} \qquad (4.140)$$

and the cell reaction is

$$Mg + 2\,MnO_2 + 2\,H_2O \longrightarrow Mg(OH)_2 + 2\,MnO(OH) \qquad (4.141)$$

Air cell

Air cell also called *air depolarised cell* is widely used in places where supply of electricity is not possible or costly and in railways. It consists of zinc anode and a porous carbon cathode immersed in 20% sodium hydroxide solution. Air enters the cell and oxygen reacts at the cathode. The electrode reactions are

$$Zn + 4\,OH^- \longrightarrow ZnO_2^{2-} + 2\,H_2O + 2\,e^- \qquad \text{(at the anode)} \qquad (4.142)$$

and

$$H_2O + [O] + 2\,e^- \longrightarrow 2\,OH^- \qquad \text{(at the cathode)} \qquad (4.143)$$

The cell reaction is

$$Zn + 2\,OH^- + [O] \longrightarrow ZnO_2^{2-} + H_2O \qquad \text{(emf 1.45 V)} \qquad (4.144)$$

Since water is formed the alkali gets diluted.

Aluminum air cell uses high purity aluminum as anode, an inert porous metal as the cathode and aqueous solution of sodium hydroxide and sodium chloride as electrolyte. The electrode reactions are

$$Al\,(s) + 3\,OH^-\,(aq) \longrightarrow Al\,(OH)_3\,(s) + 3\,e^- \qquad \text{(at the anode)} \qquad (4.145)$$

and

$$H_2O + [O] + 2\,e^- \longrightarrow 2\,OH^- \qquad \text{(at the cathode)} \qquad (4.146)$$

and the net reaction may be represented as

$$4\,Al + 3\,O_2 + 6\,H_2O \longrightarrow 4\,Al(OH)_3 \qquad (4.147)$$

The electrode reactions are

$$\mathrm{Pb} \longrightarrow \mathrm{Pb}^{2+} + 2\,\mathrm{e}^- \qquad \text{(at the negative electrode)} \tag{4.162}$$

and

$$\mathrm{PbO_2} + 4\,\mathrm{HClO_4} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Pb(ClO_4)_2} + 2\,\mathrm{ClO_4}^- + 2\,\mathrm{H_2O} \tag{4.163}$$

The overall cell reaction is

$$\mathrm{PbO_2} + \mathrm{Pb} + 4\,\mathrm{HClO_4} \longrightarrow 2\,\mathrm{Pb(ClO_4)_2} + 2\,\mathrm{H_2O} \tag{4.164}$$

The emf of the cell depends on the concentration of the perchloric acid, for 50% perchloric acid preferred at low temperatures is 1.92 V at –50° C. With fluoboric acid as the electrolyte the emf of the cell is 1.86 V. The cell cannot be charged.

Silver peroxide-zinc alkaline cell: The primary cell uses silver oxide and zinc electrodes with sodium or potassium hydroxide electrolyte kept separately. The cell may be represented as

$$\mathrm{Ag} \mid \mathrm{AgO} \mid \mathrm{KOH}\ (25\%\ \text{aq. soln.}) \mid \mathrm{Zn}$$

Since the silver oxide is soluble in the electrolyte the cell has a short shelf life and can be used for one-shot purposes. The reactions occurring at the electrodes and in the cell may be represented as

$$2\,\mathrm{AgO} + \mathrm{H_2O} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Ag_2O} + 2\,\mathrm{OH}^- \qquad \text{(at the positive electrode)}$$

$$\mathrm{Ag_2O} + \mathrm{H_2O} + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag} + 2\,\mathrm{OH}^- \tag{4.165}$$

$$\mathrm{Zn} + 2\,\mathrm{K}^+ + 4\,\mathrm{OH}^- \longrightarrow 2\,\mathrm{K_2ZnO_2} + 2\,\mathrm{H_2O} + 2\,\mathrm{e}^- \ \text{(at the negative electrode)} \tag{4.166}$$

The cell has a working voltage of about 1.35 V with a high operating current density.

Fused electrolyte cell

The cell consists of magnesium and a mixture of manganese dioxide and carbon (acetylene black) as electrodes and solid electrolytes having low melting temperatures such as sodium hydroxide, potassium hydroxide, sodium nitrate, lithium nitrate or potassium nitrate. The cell is heated by an external source to fuse the electrolyte and activate the cell. The cell reaction may be represented as

$$\mathrm{Mg} + 2\,\mathrm{MnO_2} + 2\,\mathrm{NaOH} \longrightarrow \mathrm{Mg\,(OH)_2} + \mathrm{Mn_2O_3} + \mathrm{Na_2O} \tag{4.167}$$

The cell has a working voltage of about 1.3 V.

Silver chloride cell

This reserve cell is a fresh water or sea water activated cell. The cell is preserved in dry state in hermetically sealed containers and activated by immersion in water just before use. The cell consists of magnesium and Ag/AgCl electrodes separated by a strip of absorbent paper. On immersion in water the cell generates about 1.4–1.5 V.

Gordon magnesium battery

The primary cell consists of magnesium and carbon electrodes with oxygen from air functioning as depolarizer at the carbon electrode. Water or an aqueous solution of potassium bromide solution is used as the electrolyte. The cell may be represented as

$$\mathrm{Mg} \mid \text{water} \quad \text{or} \quad \mathrm{KBr\,(aq)} \mid \mathrm{O_2\,(g)} \mid \mathrm{C}$$

Oxidation of magnesium to magnesium ions occurs at the negative (Mg) electrode and oxygen from air is consumed to form water at the carbon electrode. The cell has an open circuit voltage of 1.6 V.

A schematic diagram of the AFC is shown in the Figure. 4.19.

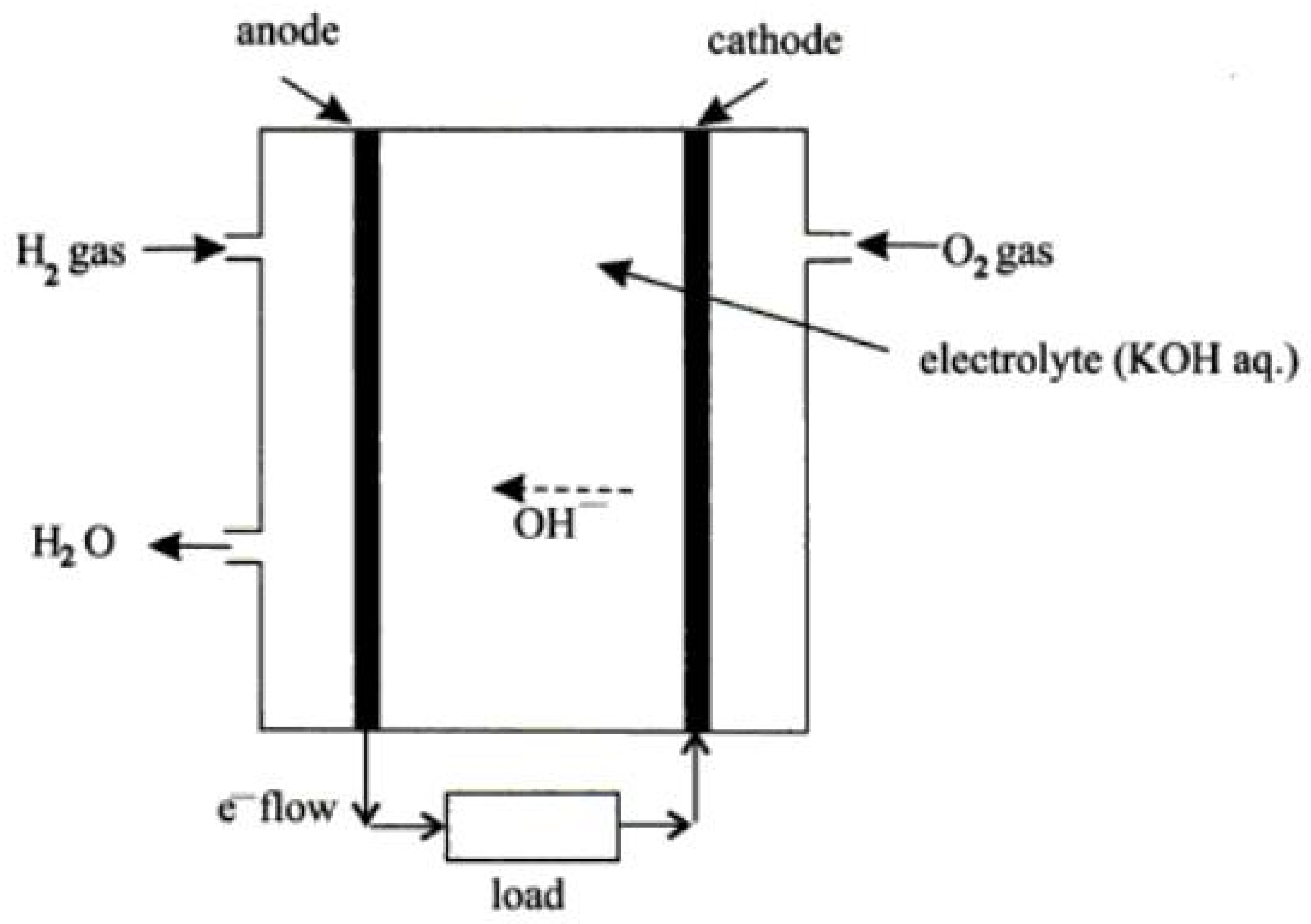

Fig. 4.19 Schematic diagram an AFC

Polymer-electrolyte-membrane fuel cell or Proton exchange membrane fuel cell (PEMFC) is also known as *ion exchange membrane fuel cell* (IEMFC) and *solid polymer fuel cell* (SPFC). A schematic diagram of the fuel cell is shown in the Figure. 4.20.

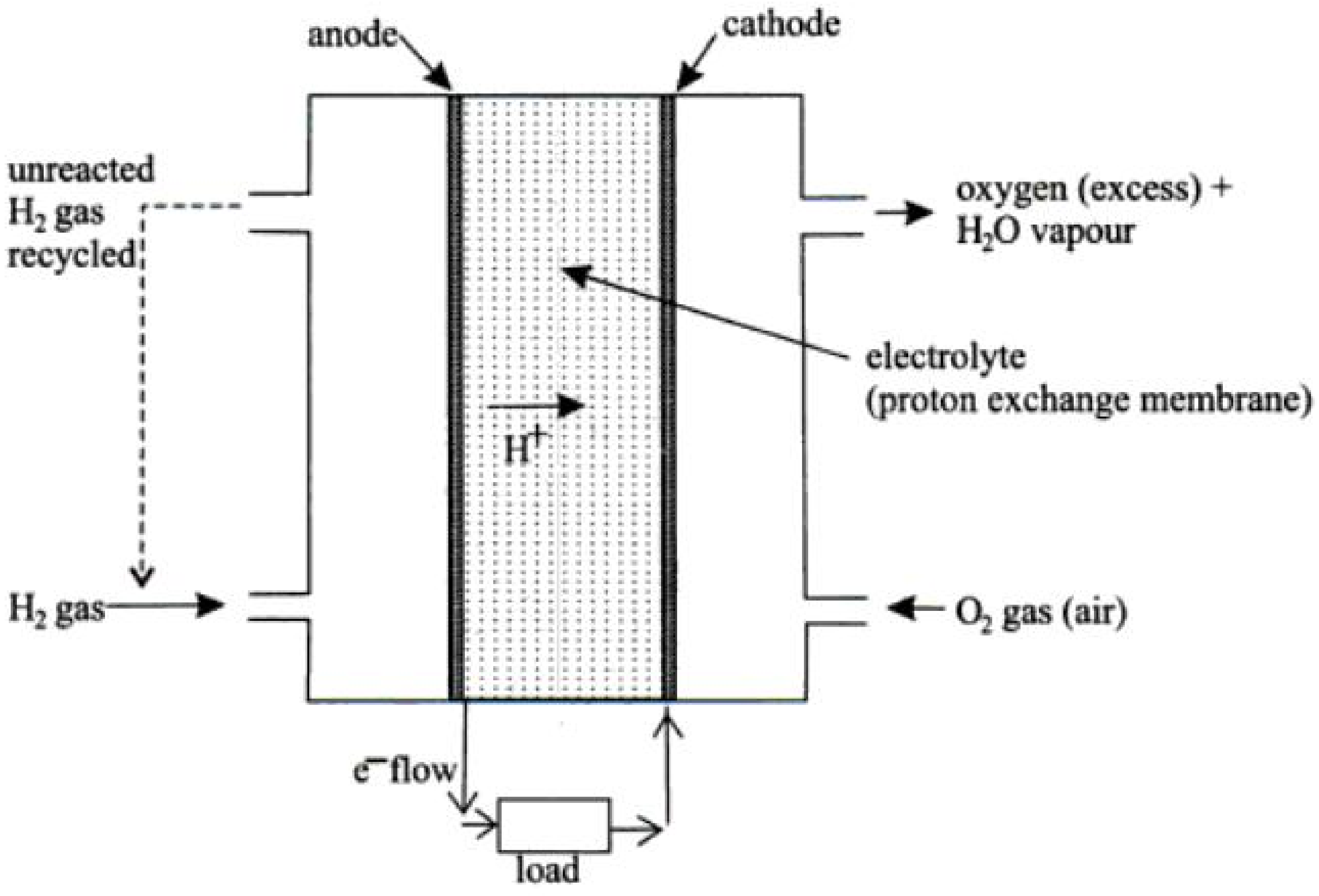

Fig. 4.20 Schematic diagram of a PEMPC hydrogen-oxygen fuel cell

Since $\Lambda_\infty = \kappa \times 1000/S$ where S is the solubility (equal to the concentration in a saturated solution)

$143.5 = (4.5 \times 10^{-5} \times 1000)/S$;

or $S = 3.136 \times 10^{-4}$ g.eq.liter^{-1}

1 mol of $Ba^{2+}\ SO_4^{2-}$ = 2 equivalents S = $3.136 \times 10^{-4}/2$

= **1.568×10^{-4} mol liter^{-1}**

Solubility in g/liter = g.eq.liter^{-1} × eq.wt.

= $3.136 \times 10^{-4} \times 129$ = **0.0202 g lites–^{1}**

◆

10. Calculate the emf of the cell $Zn|Zn^{2+}$ (0.2 M) $||Cu^{2+}$ (0.5 M) | Cu at 25° C.

Solution:

$E_{Zn} = E^0_{Zn} - 0.059/2 \log 0.2$

$= 0.76 - 0.0295 \times (-0.7) = 0.78$ V

$E_{Cu} = E^0_{Cu} - 0.059/2 \log (1/0.5)$

$= 0.34 - 0.0295 \times (-0.7) = 0.36$ V

$E_{cell} = 0.36 + 0.78 = \mathbf{1.14\ V}$

◆

11. Calculate the thermodynamic parameters for the reaction $Zn + FeSO_4 = ZnSO_4 + Fe$. The temperature coefficient is – 0.25 mV/deg. The reduction potentials E^0 for Zn and Fe are – 0.76 V and – 0.44 V respectively.

Solution:

In the cell oxidation of Zn and reduction of Fe^{2+} occur.

Hence $E_{cell} = 0.76 - 0.44 = 0.32$ V

Since E_{cell} is positive the reaction is spontaneous.

$\Delta G^0 = -nEF = -2 \times 0.32 \times 96500$

$= -61760$ J or **– 61.76 kJ/mol** (– 258 kcal/mol)

$\Delta H = nEF + nFT\,(\delta E/\delta T)$

$= -61.76 + (2 \times 96500 \times 298)(-0.25 \times 10^{-3})/1000$

$= -61.76 - 14378.5/1000 = \mathbf{-14.44\ kJ/mol}$

$\Delta S = \Delta H - \Delta G/T = 0.159$ kJ/K or **+ 159 J/K**

◆

12. Construct the cell and calculate the emf for the reaction

$Zn\,(s) + Fe^{2+}\,(0.005\ M) \rightleftarrows Zn^{2+}(0.01\ M) + Fe(s)$

(AU, Jan. 2005)

Solution:

Cell is represented as

Zn (s) + Fe^{2+} (0.005 M) || Zn^{2+} (0.01 M)/Fe

The $E^0_{Zn/Zn^{2+}} = 0.76$ V; $E^0_{Fe^{2+}/Fe} = -0.44$ V

$E_{cell} = E^0_{cell} - 0.059/2 \log [Zn^{2+}]/[Fe^{2+}]$

$= (0.76 - 0.44) - 0.059/2 \log (0.01/0.005)$

$= 0.32 - 0.0088 = \mathbf{0.311\ V}$

◆

13. State whether $Ag|Ag^+$ (0.01 M) || Ag^+ (1.0 M)|Ag constitutes a cell? (AU, Jan. 2005)

Solution:

The cell is an example of a concentration cell, the cell emf is given by eq 4.101

$E_{cell} = 0.059/1 \log 1/0.01 = 0.118$ V

The E_{cell} is positive, hence

$Ag|Ag^+$ (0.01 M) || Ag^+ (1.0 M)|Ag constitutes a cell

◆

14. The emf of a standard cadmium cell at 298 K is 1.01832 V and the temperature coefficient of the emf of the cell is -5×10^{-5} V/K. Calculate ΔG, ΔH and ΔS for the cell reaction. (AU May 2005)

Solution:

The cell is represented as

12.5% Cd in Hg | 3 $CdSO_4$. 8 H_2O (s) || $CdSO_4$ (saturated solution)Hg_2SO_4 | Hg

$\Delta G = -nFE = -2 \times 96500 \times 1.101832$

$= \mathbf{-196535.76\ J = -196.5\ kJ}$

$\Delta S = nF\,(\partial E/\partial T)_p = 2 \times 96500 \times 9 - 5 \times 10^{-5}$

$= \mathbf{-9.65\ J/K}$

$\Delta H = \Delta G + T\Delta S = -196535.76 + (298 \times -9.65)$

$= \mathbf{-199411.46\ J = -199.4\ kJ}$

◆

Review Questions

1. Distinguish between electronic and electrolytic conductors. Write a note on the changes that occur when direct current is passed through electrolyte solutions.
2. State Faradays's laws of electrolysis and their significance.
3. What is transference number? How is it determined?
4. Define the terms specific resistance, specific conductance and equivalent conductance.

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(vii) *Activation energy for desorption*: Physisorbed ecules can be easily desorbed by lowering the pressure at a given temperature as the activation energy for desorption is quite low. Thus physisorption is reversible. Chemisorption on the other hand is irreversible and the adsorbed gas cannot be desorbed simply by decreasing the pressure at the same temperature. It has a very high activation energy for desorption as chemisorbed ecules are held by relatively strong valence forces.

5.3.3 Adsorption isotherms

The relation between the amount of gas adsorbed by a solid and the equilibrium pressure or concentration at a given temperature is called an adsorption isotherm. It is obtained by plotting the adsorbate concentration in the solid phase as a function of pressure of the gas. Five general types of adsorption isotherms have been observed experimentally in the adsorption of gases by solids as shown in the Figure 5.1.

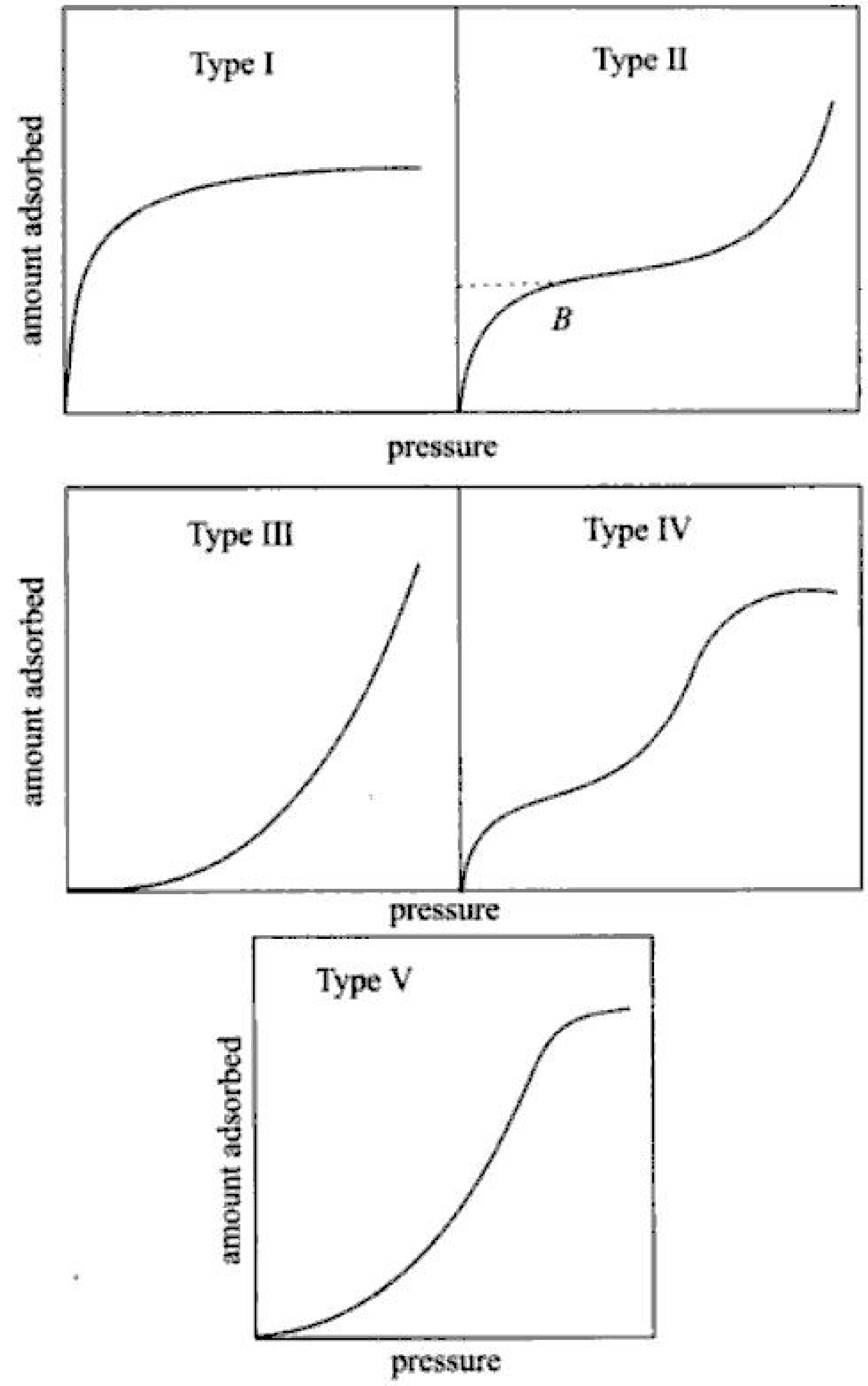

Fig. 5.1 Different types of adsorption isotherms

particular reactant. The overall order n of the reaction is the sum of the exponents of the concentration terms in the rate equation.

Overall order of the reaction $n = x + y + x$

The order of a reaction is not related to the stoichiometry and hence cannot be predicted on the basis of the stoichiometric equation. The order of a reaction can only be determined experimentally and it may have values of zero, fractions or integers.

Molecularity of a reaction is a theoretical concept and cannot be predicted from the stoichiometry of the reaction. It is defined as *the minimum number of the reactant species which participate in the slowest or the rate-determining step of a sequence of elementary reactions that determines the overall rate of the reaction.* Molecularity is always a whole number and it can never be negative, zero or a fraction. It is necessary to know whether the reaction occurs in a single step or in multi-steps so that the mechanism of the reaction can be ascertained and the molecularity of the reaction can be arrived at. In order to postulate a mechanism for a reaction it is necessary to determine the order of the reaction experimentally and the rate expression for the slowest step (rate-determining step) of the proposed mechanism must account for the observed orders in the reactants and products.

6.4 Rate Expressions of Different Orders

The order of a chemical reaction varies depending on the nature of the reactants and other factors. The reaction may be of any order zero, first, pseudo-first, second, third or fractional. The order of a reaction is determined by determining the rate of the reaction under specified conditions and deducing a rate expression which fits the experimental data. In general a rate expression provides information on how the rate of a reaction is affected by changes in the concentrations of the reactants, the reaction being carried out at a constant temperature in a thermostat and a constant composition of the solvent medium. Under such conditions the concentrations of some or all of the reactants may influence the rate of the reaction. Sometimes the products also influence the rate. If the formation of product(s) increases the reaction is said to be *autocatalytic*. In contrast the formation of product(s) will be retarded in an *autoinhibition* reaction. The reaction rate will be increased by a *catalyst* which is neither a reactant nor a product and an *inhibitor* on the other hand will decrease the rate of a reaction.

In general a rate expression is written as given by Eq. 6.6

$$v = \frac{-d[R]}{dt} = \frac{d[P]}{dt} = kC^n \tag{6.6}$$

where v is the rate expressed in mol liter^{-1}s^{-1}, C represents the concentration of the reactant R or product P in mol liter^{-1} and the rate constant k depends on the order of the reaction n and is given in units of mol $^{(1-n)}$ liter $^{(n-1)}$ s^{-1}.

6.4.1 First order reactions

In a first order reaction the rate of the reaction is determined by the concentration of a single reactant species even when more than one reactant is present. A first order reaction may be represented as

$$\mathrm{A} \longrightarrow \text{products} \tag{6.7}$$

The rate equation is $(-dC_A/dt) = k\,C_A$ (6.8)

Assuming that the initial concentration of the reactant A is a and x is the concentration after time t. Then $C_A = (a - x)$ at time t.

Since $K_c = k_f/k_r$ (ratio of the rate constants of the forward and reverse reactions), and $\Delta E = E_f - E_r$ Eq. 6.33 may be written as

$$\frac{d\ln k_f}{dT}-\frac{d\ln k_r}{dT} = \frac{E_f}{RT^2}-\frac{E_r}{RT^2} \tag{6.34}$$

In general it may be written that

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} \tag{6.35}$$

Rearranging the above equation as $d\ln k = (E/R)\ (dT/T^2)$ and integrating gives

$$\ln k = -\frac{E}{RT} + \text{constant} \tag{6.36}$$

provided E is a constant. The above equation may be written as 6.37 and is known as Arrhenius equation.

$$k = A\exp(-E/RT) \tag{6.37}$$

where k is the rate constant, A is called the frequency factor or pre-exponential factor, R is the gas constant (in cal/mol/deg) and E is called the *energy of activation*. Mathematically A is the rate constant k_∞ at infinite temperature. The units of k and A are the same while E/RT is dimensionless. The exponential term $e^{-E/RT}$ (same as the Boltzmann expression) gives the fraction of the total number of molecules having energy in excess of the value E. Arrhenius put forward the concept of *activation energy* stating that reactant molecules must be activated so that they acquire a minimum threshold energy E called the energy of activation before they react. The process of activation is endothermic and reaction occurs only between activated molecules and hence the rate of a reaction increases with temperature. A schematic representation of the activation energy is shown as the peak in the potential energy curve in the Figure 6.2.

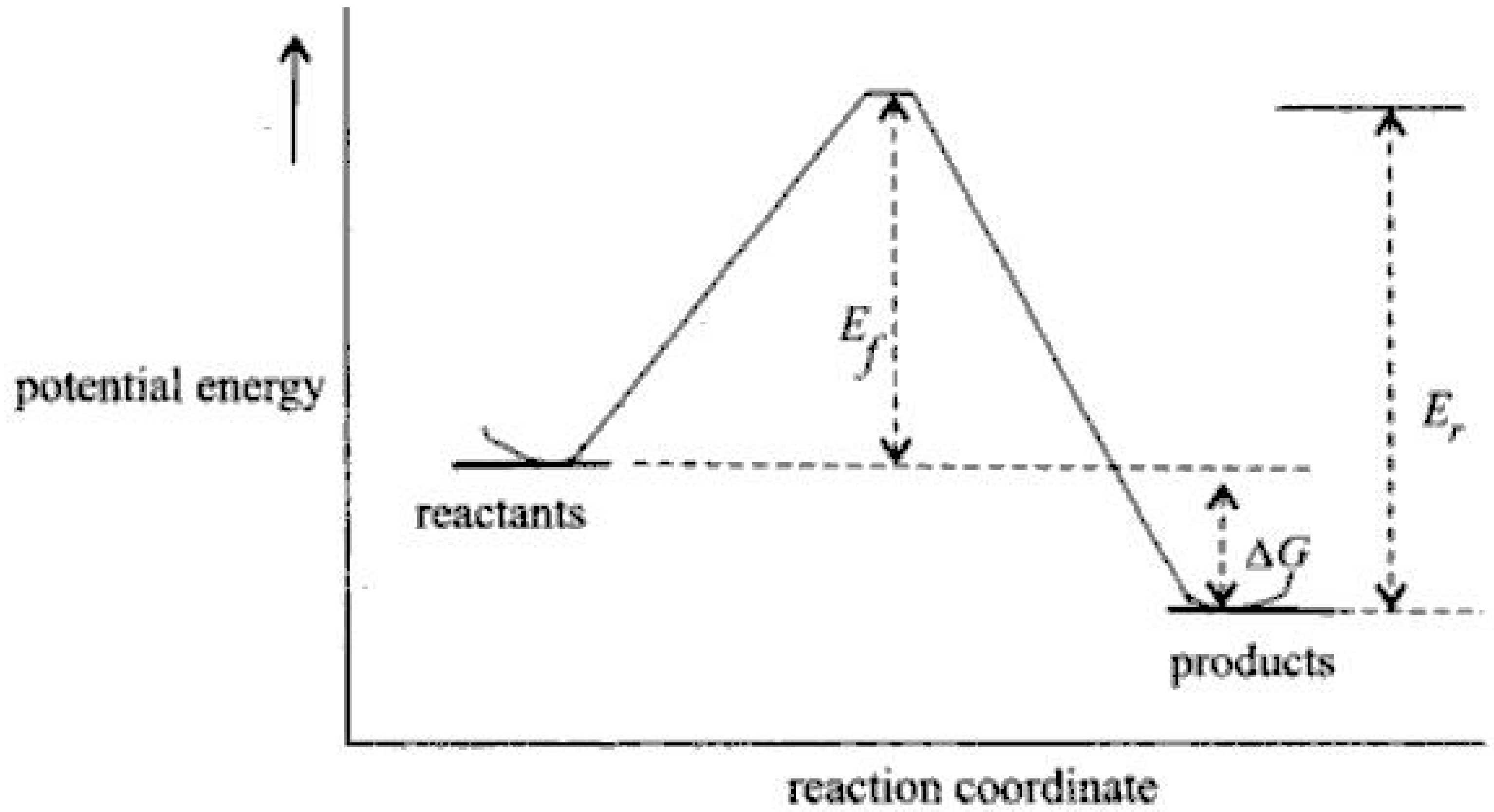

Fig. 6.2 Potential energy changes during a reaction

The energy of activation for a reactant is the average minimum energy over the average energy of the reactant molecules which must be acquired by the molecules before they can react. The reactant molecules on gaining the energy of activation form an activated complex which has the maximum

where $(a - x)$ and x are the concentrations of the reactant and the product respectively
At equilibrium $- d[A]/dt = 0$ hence

$$k_1 (a - x_e) = k_{-1} x_e \qquad (6.55)$$

where x_e is equilibrium concentration of the product B and has a definite value depending on the value of a and temperature. The equilibrium constant K for the reaction is given as

$$K = \frac{k_1}{k_{-1}} = x_e/(a - x_e) \qquad (6.56)$$

The rate constant for the reverse reaction is given as

$$\begin{aligned} k_{-1} &= k_1 (a - x_e)/x_e \\ &= (k_1 a/x_e) - k_1 \end{aligned} \qquad (6.57)$$

The reaction behaves like a simple first order reaction, the equilibrium concentration x_e replacing the initial concentration of the reactant and the rate constant being $k_1 a/x_e$.

The rate constants for the forward and reverse reactions may be evaluated from the Eq. 6.56 and 6.58 respectively.

$$k_1 a/x_e = k_1 + k_{-1} \qquad (6.58)$$

A typical example of an equilibrium reaction involves the phenomenon of *mutarotation* in which optical rotation of an enantiomer changes with time as in the case of glucose and lactose solutions due to reversible interconversion of the isomers. The formation of HI and its decomposition and the oxidation of nitric oxide to nitrogen dioxide are other examples of opposing reactions.

6.8.2 Consecutive reactions

These are reactions in which the products of the first reaction become the reactants in the subsequent reaction. A consecutive reaction and the corresponding concentrations of the species may be represented as

$$\begin{array}{ccccc} A & \xrightarrow{k_1} & B & \xrightarrow{k_2} & C \\ (a - x) & & y & & z \qquad x = (y + z) \end{array} \qquad (6.59)$$

Assuming the reaction to follow first order kinetics, the rate of decomposition of A is given by

$$- d[A]/dt = dx/dt = k_1[A] = k_1(a - x) \qquad (6.60)$$

The concentration of B depends on the rate of disappearance of A as well as on the rate of conversion of B into C.

$$d[B]/dt = dy/dt = k_1[A] - k_2[B] = k_1(a - x) - k_2 y \qquad (6.61)$$

The concentration of C depends on the rate of conversion of B

$$d[C]/dt = dz/dt = k_2[B] = k_2 y \qquad (6.62)$$

In the absence of B and C at the beginning of the reaction the reaction should follow a first order decay as given by

$$(a - x) = ae^{-k_1 t} \qquad (6.63)$$

Substituting the above equation into the equation 6.61 gives

$$dy/dt = k_1 \{ae^{-k_1 t}\} - k_2 \qquad (6.64)$$

On integrating the above equation

$$y = \frac{k_1 a}{k_2 - k_1}\left\{e^{-k_1 t} - e^{-k_2 t}\right\} \qquad (6.65)$$

of a substance called catalyst which is recovered at the end of the reaction. The phenomenon is called *catalysis*. A catalyst is a substance which modifies the rate of a reaction but remains unaltered and hence recovered at the end of the reaction.

6.9.1 Characteristics of catalysed reactions

A small amount of catalyst is sufficient to bring about an appreciable change in the rate of the reaction. For example few milligram quantity of platinum powder is sufficient to catalyse the combination of large amounts of hydrogen and oxygen to form water.

A catalyst is considered to be a positive catalyst when it increases the rate of a reaction and a negative catalyst or inhibitor if it decreases the rate of the reaction. For example ethanol retards the decomposition of hydrogen peroxide to water and oxygen.

A product of the reaction itself may serve as a catalyst. Such a phenomenon is known as *autocatalysis*. For example, in the oxidation of oxalic acid by acidified potassium permanganate the rate increases as the reaction proceeds due to autocatalysis by manganese(II) ions formed by the reduction of permanganate ions. Ester hydrolysis is yet another reaction autocatalysed by the acid formed.

A catalyst remains unaltered at the end of the reaction in mass and chemical composition. However a change in the physical state may occur. For example, in the oxidation of ammonia to nitric oxide platinum gauze used as catalyst becomes coarse at the end of the reaction. Similarly coarse particles of MnO_2 used in the decomposition of potassium chlorate to prepare oxygen become finely divided powder at the end of the reaction.

The catalyst definitely participates in the reaction as evidenced from the apparent changes in the nature of the catalyst. The possible mechanistic steps in the decomposition of $KClO_3$ catalysed by MnO_2 may be represented as

$$2\,KClO_3 + 2\,MnO_2 \longrightarrow 2\,KMnO_4 + Cl_2 + O_2 \tag{6.75}$$

$$2\,KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2 \tag{6.76}$$

$$K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2 \tag{6.77}$$

Supporting evidence for the above steps comes from the fact that the oxygen contains traces of chlorine and the formation of $KMnO_4$ as indicated by the appearance of pink colour when the reaction mixture is cooled in the early stages.

During the course of the reaction the concentration of the catalyst is not altered and hence it is not included in the rate expression. The importance of the catalyst concentration may be demonstrated by the dependence of the apparent rate of a catalysed reaction as a function of the catalyst concentration. For a general reaction between A and B involving a catalyst C, the rate expression may be written as

$$d[P]/dt = k\,[C][A][B] = k'\,[A][B] \tag{6.78}$$

k' represents the apparent rate constant and is a product of the true rate constant k and the concentration of the catalyst.

The catalyst does not initiate a reaction, it only accelerates a reaction. In general the feasibility of a reaction is indicated by the free energy change ΔG being negative for the reaction which remains the same in the presence or absence of a catalyst as shown by the potential energy profile in the Figure 6.5.

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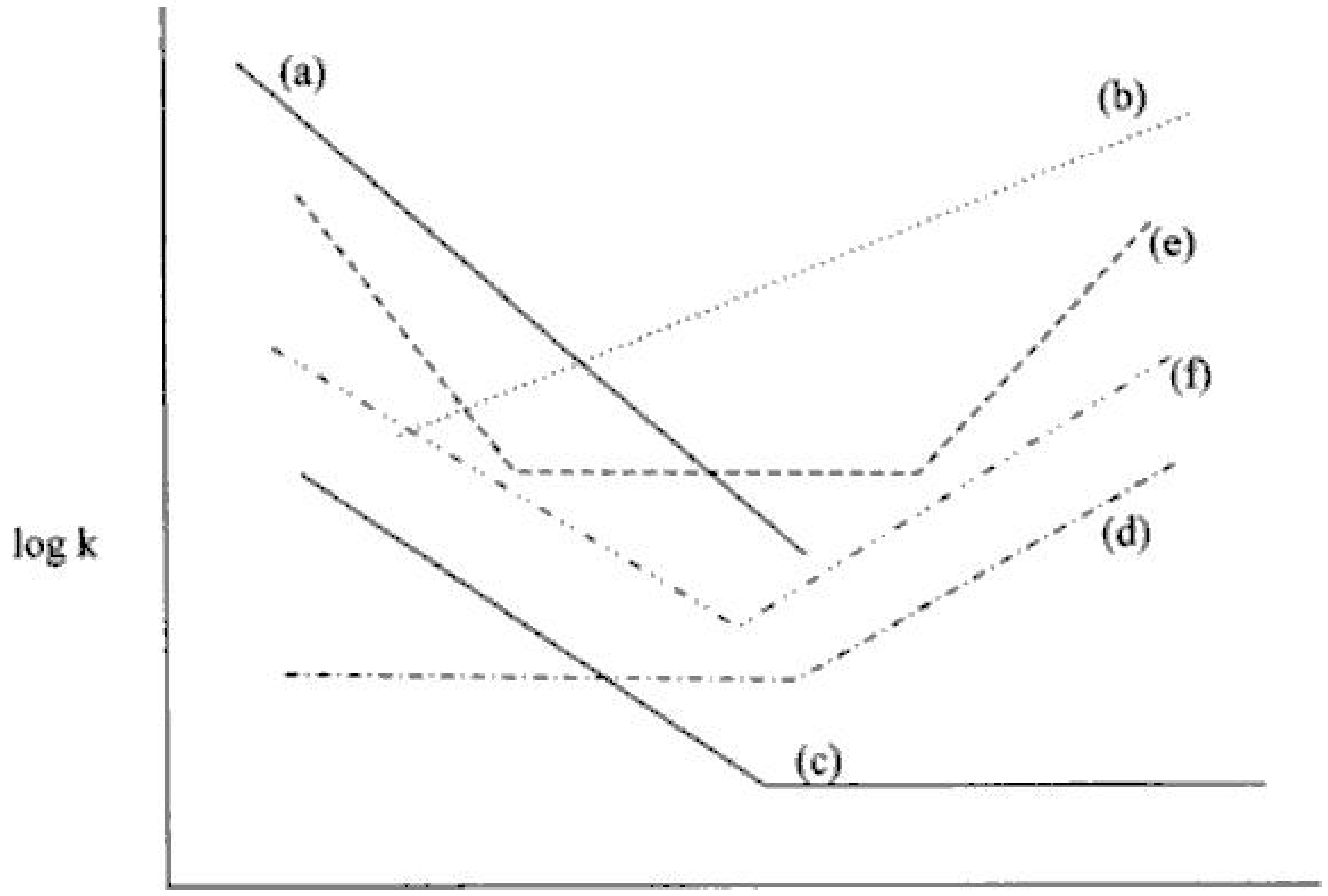


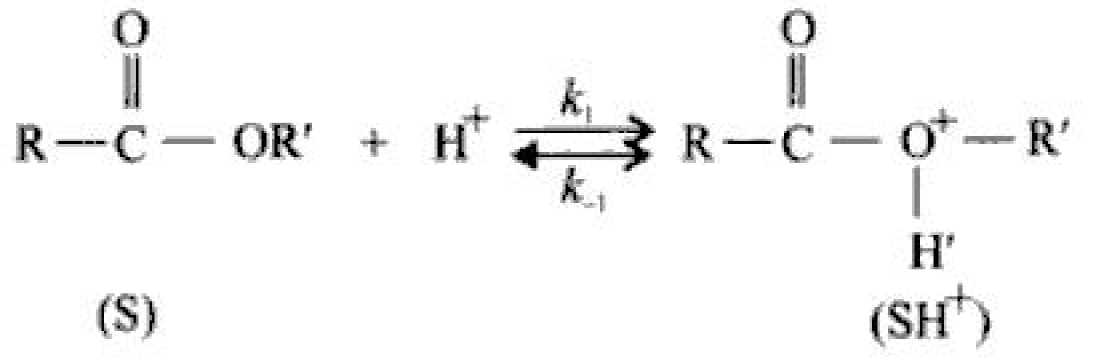
Fig.6.7 Skrabal diagrams showing the relationship between log k and pH

Using Bronsted's definition of acids and bases, an acid may be considered to act as a catalyst by virtue of its proton losing capacity while a base acts as a catalyst by virtue of its ability to abstract protons. Thus acid catalysis involves the transfer of a proton from the catalyst BH^+ (acid) to the reactant S to form the activated complex SH^+ which subsequently forms the products

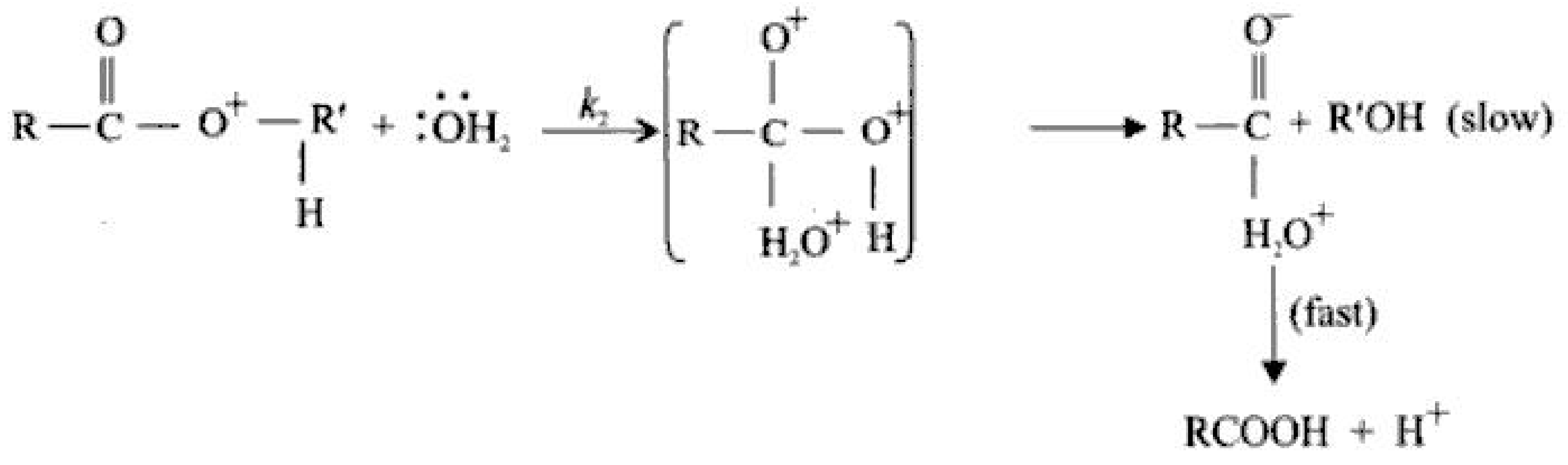
$$S + BH^+ \rightleftharpoons SH^+ + B \qquad (6.93\ a)$$

$$SH^+ + B\ (\text{or } H_2O) \longrightarrow P + BH^+\ (\text{or } H_3O^+) \qquad (6.93\ b)$$

The detailed mechanistic steps in the specific acid catalysed reaction of hydrolysis of an ester may be shown as



$$\underset{(S)}{R-\overset{\overset{O}{\|}}{C}-OR'} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(SH^+)}{R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H'}{|}}{O^+}-R'} \qquad \text{(fast)} \qquad (6.94\ a)$$



$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{O^+}-R' + :\ddot{O}H_2 \xrightarrow{k_2} \left[R-\underset{\underset{H_2O^+}{|}}{\overset{\overset{O^+}{|}}{C}}-\underset{\underset{H}{|}}{O^+}\right] \longrightarrow R-\underset{\underset{H_2O^+}{|}}{\overset{\overset{O^-}{\|}}{C}} + R'OH\ \text{(slow)} \qquad (6.94\ b)$$

$$\xrightarrow{\text{(fast)}} RCOOH + H^+ \qquad (6.94\ c)$$

The rate of the reaction is given as

$$v = k_2[SH^+] \quad \text{or} \quad v = \frac{k_1k_2[RCOOR'][H^+]}{k_{-1}+k_2} \qquad (6.95)$$

6.9.6 Industrial applications of heterogeneous catalysts

A few industrial applications of heterogeneous catalysts are listed in the Table 6.1

Table 6.1 Heterogeneously catalysed industrial processes

Process	*Feed stock*	*Catalyst*	*Products*
1. Refinery processes			
Cracking	Crude petroleum	Faujasite	Gasoline, heating oil
Cracking	Kerosene and residues of atmospheric distillates of crude oil	Al_2O_3/SiO_2	Gasoline
Hydrocracking	Crude oil + hydrogen	Faujasite	Kerosene
Hydrocracking	Vacuum distillates of crude oil	Pd/zeolites, Ni/SiO_2- Al_2O_3 $MoO_3/CoO/$ Al_2O_3	Gasoline and other fuels
Hydrodesulphurization	Crude oil fractions	$CoS/MoS_2/Al_2O_3$ $NiS/WS_2/Al_2O_3$	Desulphurized fuels
Reforming	Naphtha	Pt/Al_2O_3	High octane gasoline, LPG, aromatics
Isomerization	Light gasoline m-xylene	Pt/Al_2O_3 ZSM-5	Isoalkanes o-p-xylenes
Oligomerization	Olefins	H_3PO_4/kieselguhr	Gasoline
Dewaxing	Middle distillate	ZSM-5, mordenite	Lubricants
2. Organic chemicals and fuels			
Hydrogenation	CO + H_2	$ZnO-Cr_2O_3$ $CuO-ZnO-Cr_2O_3$	Methanol
Hydrogenation	Edible oils	Ni/Cu	Fats
Dehydrogenation	Ethylbenzene	Fe_3O_4(Cr,K oxides)	Styrene
Dehydrogenation	Benzene	Cr_2O_3/Al_2O_3	Butadiene
Alkylation	Benzene + ethene	ZSM-5	Styrene
Disproportionation	Toluene	ZSM-5	Xylene, benzene
Methanol-to-gasoline (MTG)	Methanol	ZSM-5	Gasoline
Methanol-to-olefin (MTO)	Methanol	ZSM-5	Olefins
Oxidation	Propene	Bi/Mo oxides	Acrolein
Oxidation	Ethene	Ag/support	Ethylene oxide
Ammoxidation	Propene	Bi molybdate	Acrylonitrile
Polymerization	Ethene	Cr_2O_3/MoO_3	Polyethylene

A large number of zeolites are known (more than 100); most of them have been prepared synthetically. As in the case of amorphous aluminosilicates, the acid strength of a zeolite increases with increasing Si : Al ratio. The surface acidity of zeolites can be tuned or tailor made to suit different reactions catalyzed by them. The concentration of acid sites, their nature and the strength of acid sites can be varied by altering the Si : Al ratio, both in the natural as well as in synthetic zeolites. Dealumination (removal of Al) is carried out by acid leaching, use of chelating agents, incorporating alkali metal ions by ion exchange or treatment with silicon tetrachloride.

Zeolites are distinguished on the basis of the geometry of the cavities and channels formed by the rigid framework of SiO_4 and AlO_4^- tetrahedra. The tetrahedra are the primary building blocks which are interconnected to form 16 possible secondary building blocks (polygons). The secondary building blocks in turn are interconnected to form hollow three-dimensional structures composed of polyhedra as tertiary building units. One of the polyhedra-the truncated octahedron, called the sodalite cage or β-cage is formed by rings of 4- and 6- tetrahedra (vide Figure 6.9).

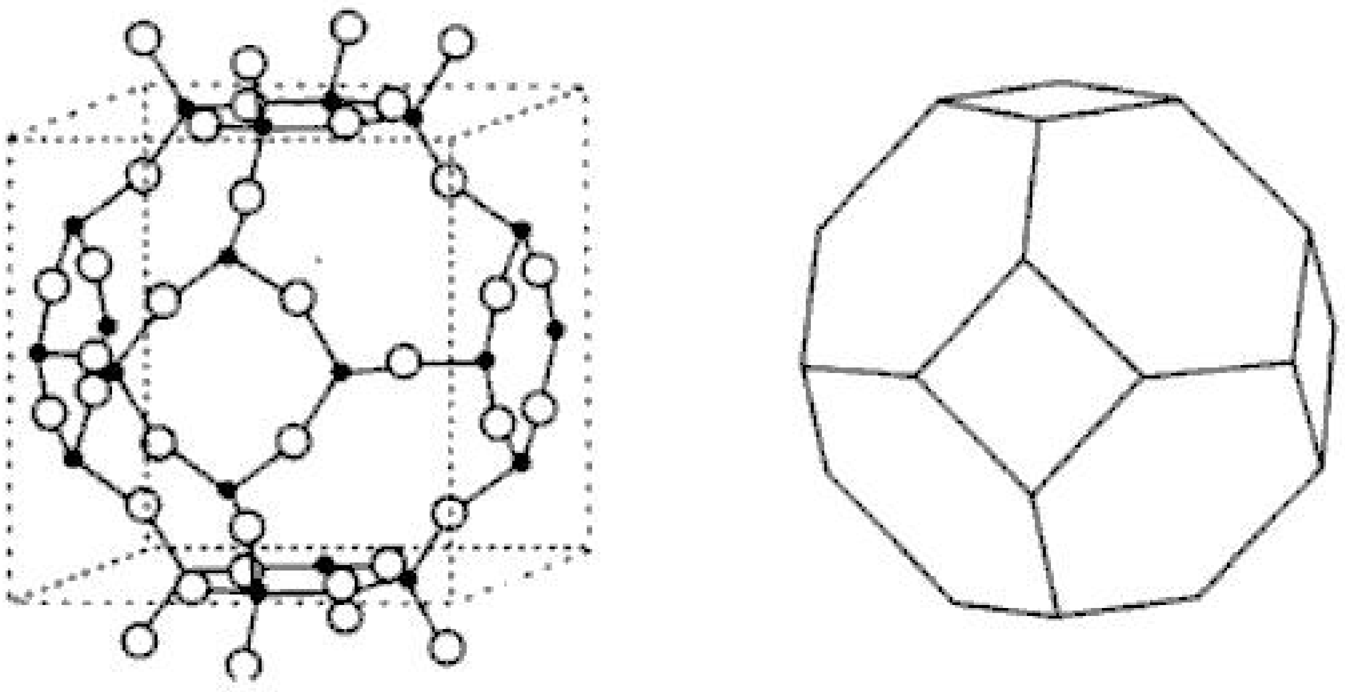


Fig. 6.9 Sodalite cage

The β-cage has an internal dia of 0.66 nm and has a six-ring opening (0.25 nm dia). Only small molecules such as H_2 or H_2O can enter this cage.

The linking of the truncated octahedra in different ways gives rise to fundamental zeolite structures. Zeolites having the sodalite cage (a) as a building block are formed by linking together through extensions of either the 4-ring (b) or the 6-ring (c) as shown in Figure 6.10.

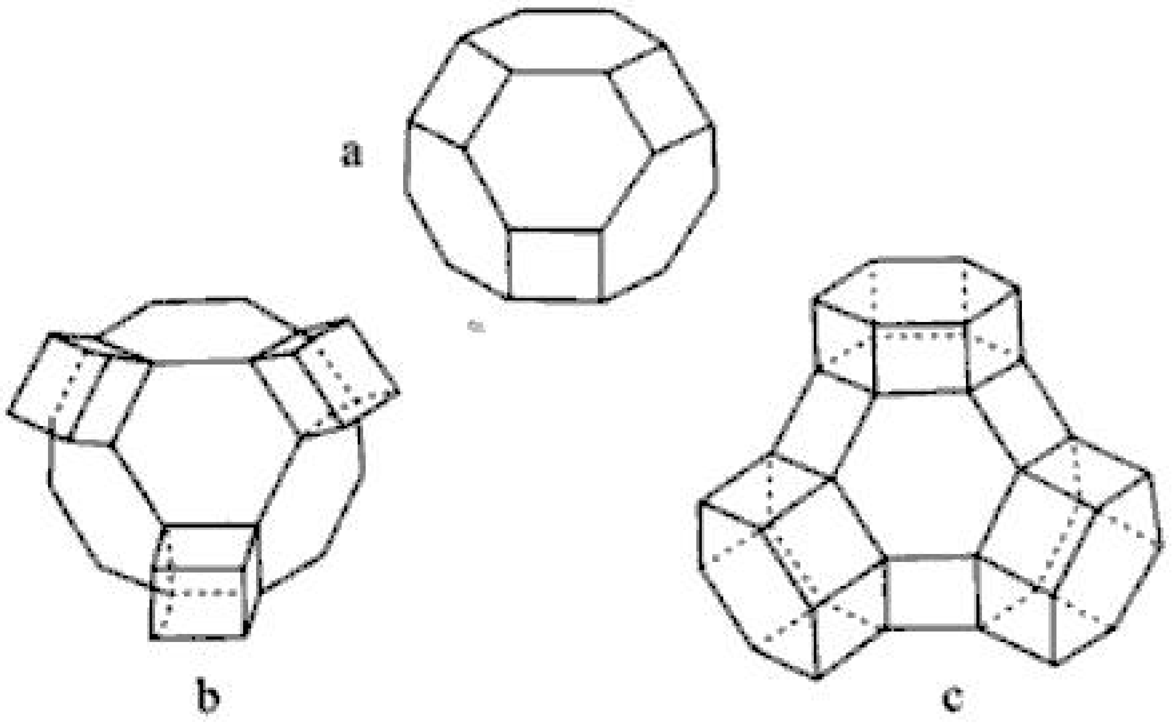


Fig. 6.10 Linking of sodalite cages

At equilibrium the two rates represented by Eq. 6.109 and 6.110 are equal.

$$k_1([E]-[ES])[S] = k_2[ES] + k_3[ES] \tag{6.111}$$

Rearranging the above equation gives

$$\frac{[S]([E]-[ES])}{[ES]} = \frac{k_2+k_3}{k_1} = K_M \tag{6.112}$$

The lumped constant K_M is called Michaelis-Menten constant. The steady-state concentration of *ES* is given by

$$[ES] = \frac{[E][S]}{K_M+[S]} \tag{6.113}$$

Since the initial rate v of the enzyme reaction is proportional to $[ES]$,

$$v = k_3[ES] \tag{6.114}$$

At high concentration of the substrate, all the enzyme *E* is present as *ES* (*ES* = *E* which is the total concentration of the enzyme) and hence the maximum rate

$$V_{\max} = k_3[E]. \tag{6.115}$$

Substituting for $[ES]$ into Eq. 6.114 from equation 6.113

$$v = k_3\frac{[E][S]}{K_M+[S]} \tag{6.116}$$

Dividing Eq. 6.116 by Eq. 6.115 and solving for v, Michaelis-Menten Eq. (6.117) for enzymatic reactions is obtained.

$$v = \frac{V_{\max}[S]}{K_M+[S]} \tag{6.117}$$

The kinetic parameters K_M and $V_{\max}$ are useful to describe the action of the enzyme on the substrate. The value of K_M depends on the substrate, pH, ionic strength, temperature and nature of the solvent used. The values of K_M are in the range of 10^{-1} to 10^{-6} M for most single substrate reactions. K_M represents the concentration of the substrate at which half the active sites on unit concentration of the enzyme are occupied, i.e., K_M = [S] at $v = \frac{1}{2} V_{\max}$. Smaller the K_M value the greater is the activity of the enzyme for a given reaction. The turnover number of the enzyme is indicated by the maximum rate $V_{\max}$. The values of K_M and $V_{\max}$ are conveniently obtained by the linear form of the equation known as Lineweaver-Burk equation.

$$1/v = (K_M/V_{\max})[S] + 1/V_{\max} \tag{6.118}$$

The Lineweaver-Burk plot of $1/v$ versus $1/[S]$ gives a straight line with a slope = $K_M/V_{\max}$ and an intercept of $1/V_{\max}$ as shown in the Figure 6.15.

The different types of specificity and other characteristics exhibited by enzymes have been explained on the basis of concept of active centre

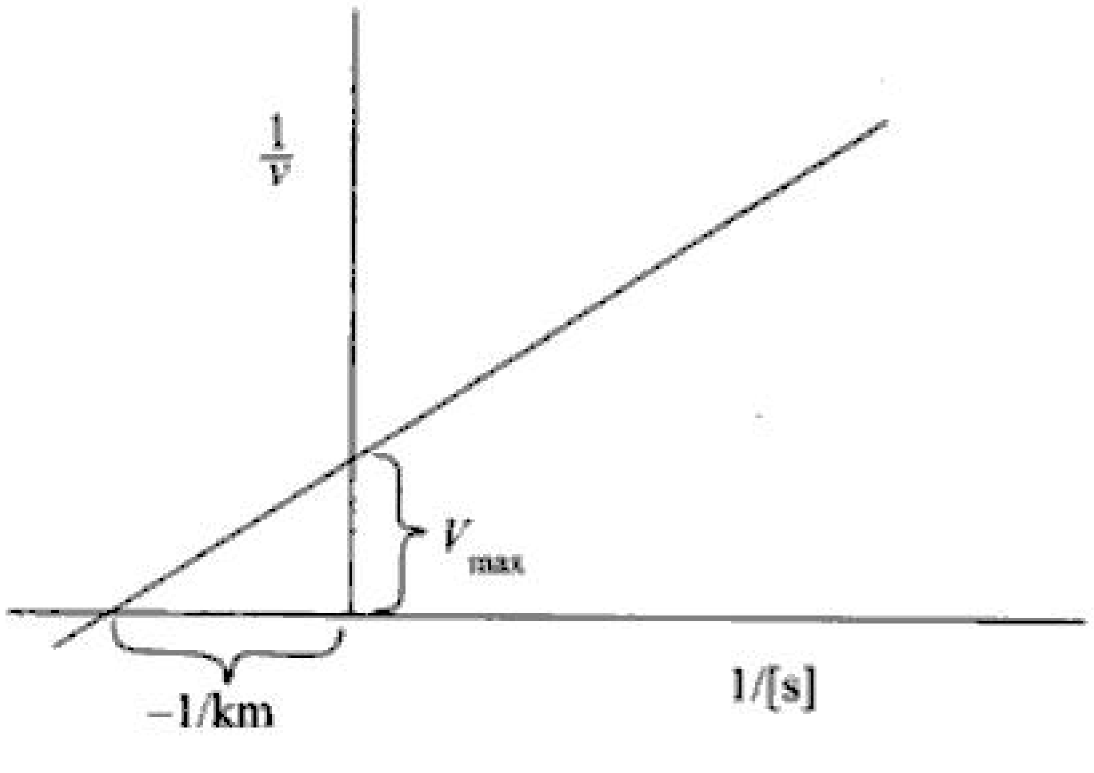


Fig. 6.15 Lineweaver-burk plot

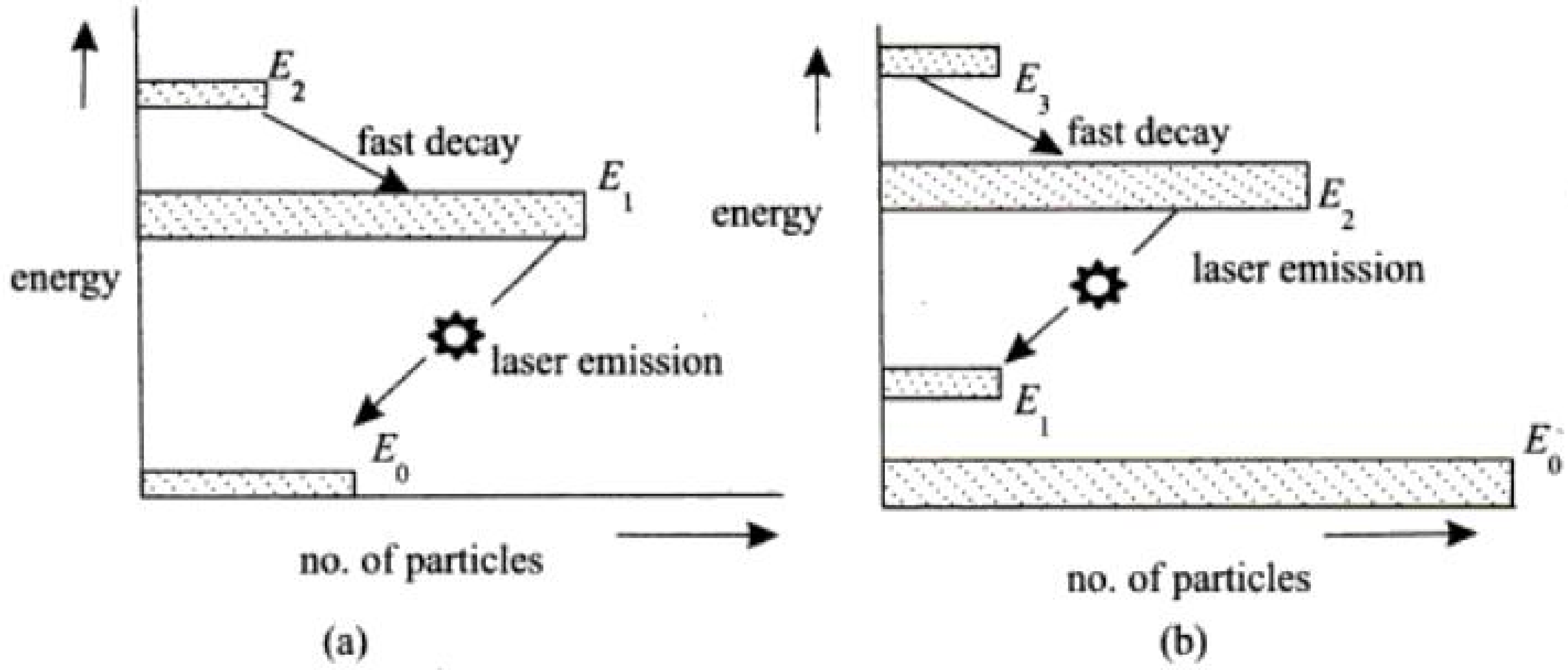


Fig. 6.16 Laser emission in (a) ruby laser based on a three level pumping requires intense pumping and (b) four-level pumping requiring pumping of much less intensity

The radiation which promotes the molecules to the higher energy state is called the pump radiation and the radiation induced to be emitted is the laser emission. The photons induced to be emitted have the same phase relationship (phase coherence) as the inducing photons. Further amplification of this coherent emission is brought about in a resonant optical cavity (optical resonator). The optical resonator consists of two highly reflecting mirrors, one a 100% reflective and another 98% reflective which allows the amplified beam to pass through either by partial transmission or through a pin hole. In the cavity the emitted light beam is passed back and forth many times through the active medium consisting of atoms, ions or molecules participating in the stimulated emission process before the amplified beam passes out. Examples of lasers include ruby laser, helium-neon laser, carbon dioxide laser, nitrogen laser, dye lasers, etc.

6.11.7 Photophysical processes of deactivation of excited stated molecules

The excited state atom or molecule is formed by absorption of light which occurs over a time span of about 10^{-15} second. The excited state molecule has a life time of about 10^{-9} second and relaxes to the ground state by a variety of pathways. The photophysical pathways of relaxation include (i) non-radiative as well as (ii) radiative pathways. The non-radiative pathways include internal conversion (*IC*) and vibrational relaxation (*VR*) through which the excited state molecule loses the energy gained by absorption of light shown as dotted lines in the Figure 6.17.

In internal conversion an excited state molecule passes from a low vibration level of S_2 to an equal energy vibration level of the S_1. The molecule in the S_1 state also may relax to the ground state S_0 by internal conversion. The process of vibrational relaxation involves the loss of vibration energy of the excited state molecule in the form of heat by collision with solvent molecules. These non-radiative pathways occur rapidly in about 10^{-12} second. Another non-radiative process involves the intersystem crossing (*ISC*) in which an electron in the excited state molecule reverses its spin. This corresponds to a spin multiplicity of 3 and the excited state molecule goes over to a triplet state, T_1. The triplet state T_1 is lower in energy than the corresponding single state S_1. A similar reverse intersystem crossing *ISC′* can take place between the lower vibrational energy levels of T_1 to equivalent vibrational energy levels of S_1.

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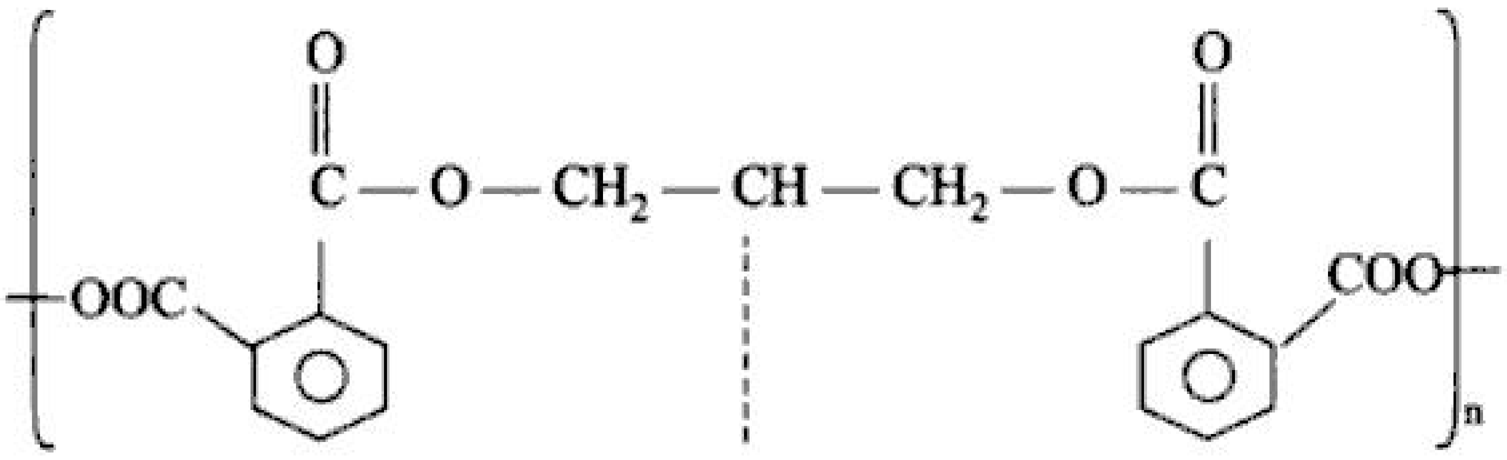
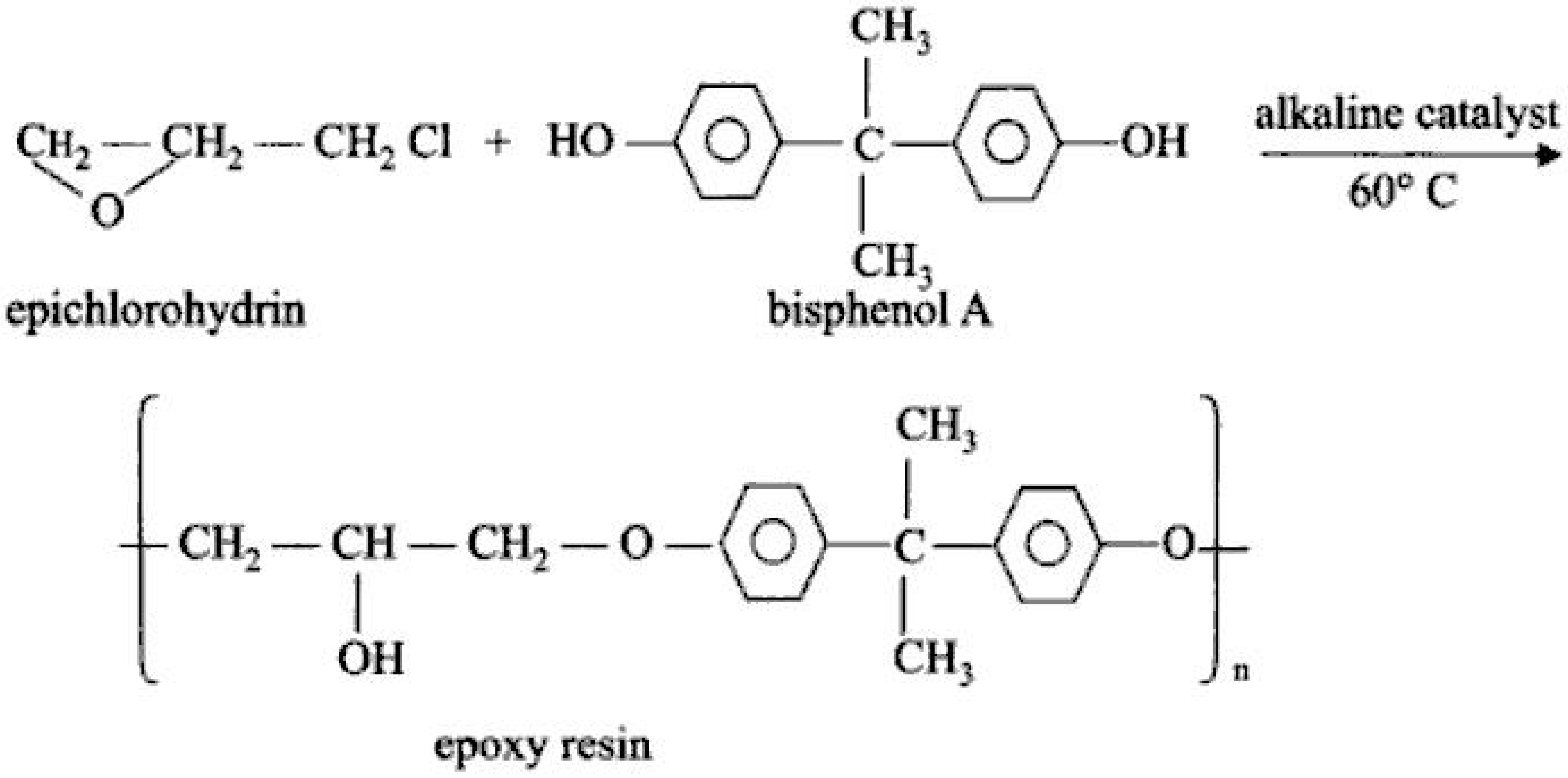


three-dimensional alkyd plastic

Alkyds find use as binders in the preparation of paints, varnishes, enamels and lacquers and in automobile parts. Because of their electrical insulating properties they are used for making switches and circuit breakers.

8.11.4 Epoxy resins

Epoxy resins are essentially polyethers obtained by the epoxidation of polyols such as bisphenol A, glycol, glycerol, resorcinol etc. with epichlorohydrin followed by polymerisation. The most common epoxy resin is derived from bisphenol A and epichlorohydrin.



(8.37)

The epoxy resins are cured by condensation with additives such as polyamines, polyamides, polysulphides, acids, acid anhydrides, phenol-formaldehyde or urea-formaldehyde resins to yield three-dimensional networks. The network structures have excellent toughness, chemical inertness and flexibility.

Epoxy resins are used in surface coatings because of their chemical inertness, toughness, good adhesion and flexibility. They are also used in the production of glass fiber reinforced articles by moulding and laminating techniques because of their good mechanical strength and electrical insulating properties.

8.12 Elastomers

Elastomers are essentially linear polymers with a distinct and characteristic elasticity. Examples include natural and synthetic rubbers.

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9 CHEMICAL METHODS OF ANALYSIS

9.1 Introduction

Chemical methods of analysis known as classical methods or wet chemical methods are traditional methods that have been in vogue for more than a century. They are still useful as they make use of simple glass ware and other common laboratory equipment for analysis of samples. The methods may be broadly classified into two groups, (i) volumetry, and (ii) gravimetry. Both these methods are macroscopic methods in that the quantity of analyte required for each estimation is in the range of 25–200 mg. These classical methods have several advantages which include (i) better precision than most of the instrumental methods; (ii) usefulness for even calibrating and validating analyses carried out using instruments; (iii) non-requirement of frequent calibration of the simple equipment used; (iv) possibility of automation; (v) preference for analysing small numbers of samples and carrying out one-off analyses; and (vi) cost-effective if not inexpensive techniques. However, the methods are labour intensive and gravimetry in particular is time-consuming. This chapter discusses the basic principles involved in these methods and the laboratory practice illustrated by a few typical examples.

9.2 Volumetry

Volumetry is based on the measurement of volumes of reactants taking part in a quantitative analysis. The method involves the use of standard solutions of reagents whose concentrations are known to determine the concentration of the analyte and simple glassware such as standard flasks, burettes, pipettes and conical flasks. The volume of the reagent required to completely react with a known volume of the analyte solution is determined by titration using a suitable indicator and hence volumetry is also known as ***titrimetry*** or ***titrimetric analysis***.

The essential conditions for any volumetric method of analysis include the following: (i) the reaction must proceed to completion rapidly; (ii) the reaction should not be complicated by additional or side reactions; (iii) there should be a detectable change (such as a sharp change in colour or formation of a precipitate) in the solution undergoing titration at the stoichiometric end point, and (iv) a suitable indicator must be available for detecting the end point.

9.2.1 Classification of volumetric methods

Based on the type of chemical reaction volumetric titrations are classified broadly into four types as (i) neutralisation or acid-base titrations, (ii) precipitation titrations, (iii) complexometric titrations, and (iv) oxidation-reduction titrations.

Neutralisation reactions involve the combination of hydrogen ions with hydroxide ions to form water. Strong acids as well as weak acids can be analysed by titrimetry using strong bases and weak bases and *vice versa*. Precipitation reactions involve the combination of ions to form sparingly soluble substances or precipitates. Precipitation reactions amenable for volumetric analysis are mostly confined to titration of halides with silver nitrate (argentometric titrations). Complexometric titrations make use of chelating agents (mostly EDTA), for forming soluble complexes with metal ions for quantitative

by the use of chemical indicators as well as instrumental methods such as conductance and potentiometric methods (Sec. 10.6).

$$AgNO_3 + X^- \longrightarrow AgX \downarrow + NO_3^- \tag{9.3}$$

$$(X^- = Cl^-, Br^-, I^- \text{ and } SCN^-)$$

Three types of chemical indicators find use in argentometric titrations. These include (i) the formation of a coloured precipitate (ii) the formation of a soluble coloured compound and (iii) an adsorption indicator.

9.4.1 Mohr's method

The method uses an indicator which forms a coloured precipitate. Quantitative estimation of chloride, bromide and cyanide ions by titrating with a standard solution of silver nitrate with a few ml of potassium or sodium chromate as indicator forms the basis of Mohr's method. At the equivalence point the yellow coloured solution of potassium chromate changes to a brick-red precipitate of silver chromate.

The titration is carried out in a neutral or faintly alkaline conditions in the pH range of 6.5 to 9 at room temperature. In acidic solutions and at higher temperatures the solubility of silver chromate increases. In alkaline solution silver hydroxide is precipitated rather than silver chromate. The procedure involves titrating a known volume of the halide solution taken in a conical flask to which 1–2 ml of potassium chromate indicator has been added, with a standard solution of silver nitrate taken in the burette. The indicator forms a red coloured precipitate of silver chromate at the end point with the first drop of excess silver nitrate added.

9.4.2 Volhard method

The method involves the formation of a red coloured complex, $[Fe(SCN)]^{2+}$, to indicate the end point. The titration of silver is carried out in nitric acid medium against a standard solution of potassium or ammonium thiocyanate taken in the burette with ferric nitrate or ferric alum as the indicator. Silver thiocyanate is precipitated quantitatively ($K_{sp} = 7.1 \times 10^{-13}$) and after complete precipitation of silver, the slight excess of thiocyanate added forms the red coloured complex species with ferric iron indicating the end of the titration. The method is more useful for the determination of chloride, bromide and iodide in acidic medium.

The procedure for the determination of chloride involves the addition of a known excess of a standard solution of silver nitrate to a known volume of chloride taken in a conical flask to precipitate the halide. The excess silver nitrate is back-titrated with a standard solution of thiocyanate. Silver chloride is more soluble compared to silver thiocyanate and during the back titration the added thiocyanate will dissolve the silver chloride precipitate. Hence nitrobenzene (~1–2 ml) is added to the silver chloride precipitate before the back titration is carried out. The added nitrobenzene forms a film protecting the silver chloride particles from interacting with thiocyanate. A few drops of ferric alum indicator are added to the conical flask and the mixture is then back-titrated against potassium or ammonium thiocyanate. At the end point after all the silver has been precipitated the added thiocyanate reacts with iron to form the red coloured solution.

9.4.3 Fajans method

The method uses an adsorption indicator to detect the end point in the titration of halides with silver. The adsorption indicator ion gets adsorbed onto the colloidal precipitate strongly, showing a different colour

The end point is the disappearance of the blue colour. Starch forms a blue coloured adsorption complex with iodine and the end point the complex is destroyed discharging the blue colour.

The procedure involves adjusting the pH of a known volume of copper(II) solution to about 4.5–5.5. A few drops of sodium carbonate is added to give a faint bluish white precipitate of copper hydroxide which is just dissolved by the addition of a few drops of dilute acetic acid to buffer the solution to the desired pH. A solution of 10% potassium iodide is added to the copper solution to precipitate cuprous iodide and liberate iodine. The liberated iodine is then titrated against a standard solution of sodium thiosulphate till the dark brown colour fades to pale yellow. About 2 ml of a 1% solution of starch is added to form the blue coloured starch-iodine complex and the titration continued till the end point, which is discharge of the blue colour.

Another example of iodometry is the determination of dissolved oxygen in water by Winkler method discussed in 14.3.4.

9.7 Gravimetry

Gravimetric methods are based on the measurement of mass of the analyte or the substance derived from the analyte using an analytical balance. Gravimetric methods may be broadly classified into two major types, namely, (i) volatilization methods, and (ii) precipitation methods. ***Volatilization method*** involves the drying or heating of a sample to determine by weighing the content of volatile and/or non-volatile components. A typical example is the determination of total dissolved solids in a sample of water wherein a known quantity of water is evaporated (volatilized off) to leave behind the residue of dissolved solids, which is weighed. Another example is the determination of carbonate or carbon dioxide content of a carbonate ore such as dolomite or magnesite in which the ore of known weight is heated to volatilize off the carbon dioxide leaving behind a residue of the metal oxide. The loss of weight in the sample ore is taken as the carbonate content of the sample. ***Precipitation method*** is more widely practiced in the case of inorganic samples and basically involves the formation of a precipitate through an appropriate reaction and weighing of the precipitate. The precipitation method is discussed in more detail in the following section.

9.7.1 Theoretical principles of precipitation method

The steps involved in the precipitation methods include: (i) conversion of the analyte into a precipitate through an appropriate chemical reaction, (ii) collection of the precipitate and washing it to free from impurities, (iii) heat treatment of the precipitate to convert it into a stoichiometric compound, and (iv) weighing the compound to calculate the amount of analyte. The steps mentioned above may be explained with the specific example of calcium. Calcium in the water soluble form of calcium chloride is precipitated as calcium oxalate by reacting with ammonium oxalate in the first step. The precipitate is collected quantitatively over a sintered glass crucible of known weight and washed in the second step. In the third step the precipitate is dried in an air oven at 110-130° C to form the stoichiometric compound of $CaC_2O_4.H_2O$ which is then weighed. The amount of calcium in the sample is calculated from the weight of the precipitate.

The gravimetric precipitation process should satisfy certain criteria to be of practical value. (i)The precipitating agent should react specifically or at least selectively with the analyte. Specific reagents are rare. (ii) The precipitate should be formed quantitatively and within a reasonably short time. (iii) The solubility of the precipitate should be small so as to achieve quantitative separation with no significant loss of analyte during subsequent treatment steps of filtering and washing.

Review Questions

1. List the wet chemical methods of analysis and their advantages.
2. What are the different types of volumetric analyses? Give examples.
3. What are primary standards? What are their characteristics? Give two examples.
4. Write a note on the theory of acid-base indicators.
5. Discuss the principles involved in the choice of indicators for acid base titrations.
6. How are the different types of alkalinity of water determined?
7. Explain the principle involved in precipitation titrations.
8. Describe the Mohr method of determination of silver.
9. How is chloride determined by Volhard method?
10. What is an adsorption indicator? How does it function?
11. What are metal ion indicators? Give examples.
12. How does eriochrome black T function as an indicator in EDTA titrations?
13. Describe how zinc is determined by direct EDTA titration.
14. How is nickel determined by back titration using EDTA?
15. How is total hardness of water determined by EDTA titration?
16. List the oxidizing and reducing agents used in redox titrations.
17. Explain the relevance of Nernst equation with reference to redox indicators.
18. How is iron determined by dichrometry?
19. Describe the procedure for the determination of copper by iodometry.
20. List the steps in the gravimetry precipitation for quantitative analysis.
21. What are precipitating agents? Give two examples.
22. How is aluminum determined gravimetrically?

Heisenberg uncertainty principle clearly states that if a system exists in an energy state over a limited time of δt seconds then the energy of that state will be uncertain to an extent of δE as given by the relationship $\delta t \times \delta E \sim h/2\pi \sim 10^{-34}$ Js. Though the energy of the lower energy level may be defined precisely ($\delta t = 0$ and $\delta E = 0$) the lifetime of the higher energy level (excited state) is less than 10^{-8} second and hence the uncertainty of δE will be about $10^{-34}/10^{-8} = 10^{-26}$ J. Thus the transition between these two states will have an energy uncertainty of δE and the broadening will occur over δv because $\delta v = \delta E/h \sim h/2\pi h\delta t \sim 1/2\pi\delta t$.

10.3 Atomic Spectroscopy

Atoms are the simplest form of matter and have only electronic energy levels without any vibrational or rotational sub energy levels. Interaction of electromagnetic radiation with atoms can result in electronic transitions only either due to *absorption* or *emission* of energy in the form of radiation. Atomic spectroscopy is primarily concerned with the absorption of energy in the form of electro magnetic radiation or the emission of radiation. Most of the atoms (almost 96–98%) normally exist at the ground state at lower and ambient temperatures and absorb energy in the form of electromagnetic radiation. The study of absorption of electromagnetic radiation by atoms is known as ***absorption spectroscopy***. The difference in energy between various electronic energy levels and hence the absorption frequencies are characteristic of individual atoms and are useful in qualitatively identifying the nature of the atom. The intensity of absorption is directly proportional to the concentration of the ground state atoms. However, it is easier in practice to measure the intensity of transmitted light (I_t) after a part of the incident light (I_0) has been absorbed by the medium. The ratio $\log(I_0/I_t) = A = kC$, where k is a constant. The relationship is known as Beer's law and is useful in quantitative analysis.

Atoms absorb energy and get excited when the electrons from the outer most valence shell acquire energy and occupy the higher energy excited states. The excited state atom is not stable and has a life time of only about a fraction of a second in the range of micro and nanoseconds. It returns to the ground state by either dissipating the energy in the form of heat to the surrounding or by emission of characteristic radiation. Excitation of ground state atoms may be achieved not only by incident electromagnetic radiation but also by other means such as thermal excitation using a flame or a high temperature plasma or electrically using dc arc and spark as well as by lasers. The study of emission of radiation by the excited state atoms (independent of the method of excitation) is known as ***emission spectroscopy***. As in absorption spectroscopy the difference in the energy levels and the emission frequencies are characteristic of the individual atoms and hence useful in the qualitative analysis. The intensity of emitted radiation (I_e) is directly proportional to the concentration (C) of the excited state atoms and hence useful in quantitative analysis as given by the equation $I_e = k'C$, where k' is proportionality constant.

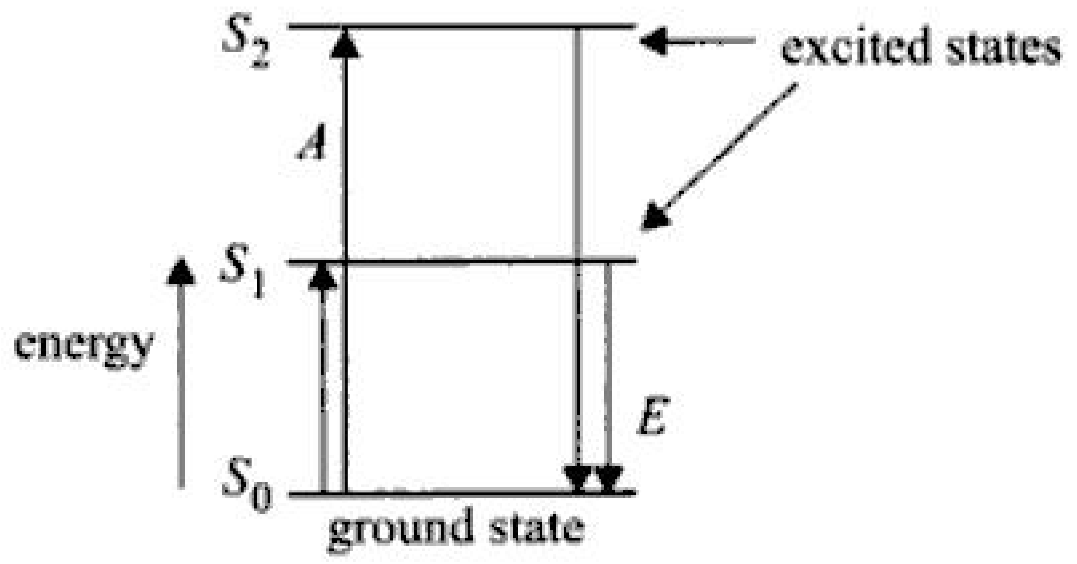

Fig. 10.2 Simplified energy level diagram of an atom

The electronic transitions during absorption or emission are discrete or quantized and hence simple line spectra are observed when free atoms absorb or emit radiation. The discrete nature of electronic transitions may be easily understood with the help of simplified energy diagram of atoms (Figure 10.2) showing absorption (A) and emission (E) of radiation.

The change in dipole moment during an electronic transition is the largest and hence uv-visible spectrometry is more sensitive for quantitative analysis compared to IR or microwave spectroscopy.

When molecules absorb energy by interacting with electromagnetic radiation the molecules go to the excited state. The excited molecules are stable only for a short time of the order of microseconds and relax to the ground state by radiative (emitting radiation) or non-radiative pathways. In non-radiative pathways the energy is converted into translational energy and evolves as heat. Radiative pathways include emission of radiation in the form of fluorescence or phosphorescence. The techniques of *fluorimetry* and *phosphorimetry* also find applications in analysis of substances.

10.4.1 UV-visible spectroscopy

The ultraviolet and visible region of the electromagnetic spectrum extends between 200 nm and 800nm (wave number range 50,000–12,000 cm^{-1}), the wavelength range 200–350 nm being the ultraviolet region and the longer wavelengths constituting the visible region. The uv-visible spectroscopy is also known as electronic absorption spectroscopy as molecules absorb radiation resulting in transitions between electronic energy levels. The principles of electronic transitions are common to both the ultraviolet and visible regions. Instruments required to record electronic transitions are also common to both the regions.

All molecules can undergo electronic transitions resulting in changes in the electronic structure. Since the energy changes involved in electronic transitions are quite large, simultaneous changes in vibrational and rotational energies of molecules also occur. The effect of these changes on the electronic absorption spectrum of a gaseous diatomic molecule may be understood by considering the potential energy diagram as shown in the Figure 10.9.

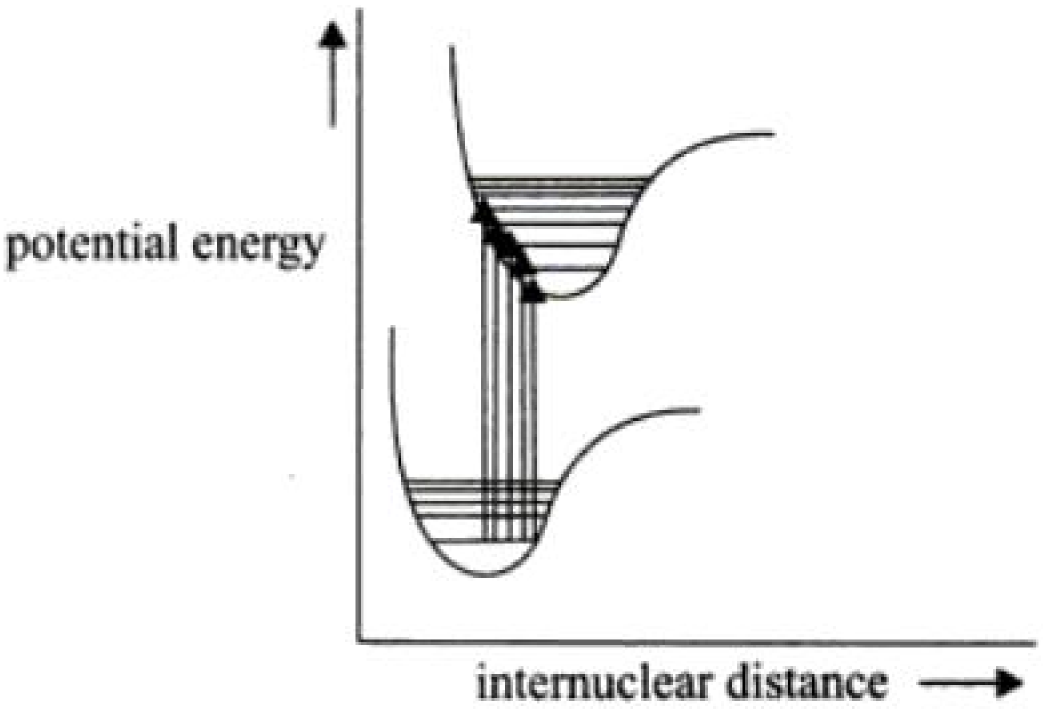

Fig. 10.9 Electronic and vibrational transitions of a gaseous diatomic molecule

The figure represents the variation of potential energy of a vibrating diatomic molecule as a function of internuclear distance. The potential energy curves of the ground and the first excited electronic states of the molecule are shown. The vibrational energy levels of the two states are indicated by horizontal lines while the rotational energy levels (sub energy levels within each vibrational level) have not been shown for simplicity. The excited state potential energy curve is displaced towards a greater internuclear distance indicating the greater equilibrium of the excited state as compared to that of the ground state. *Franck-Condon principle* states that *electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.* Hence the electronic transitions may be represented by vertical lines between the ground and the first excited state electronic levels. At room temperature almost all the molecules will be in the ground state electronic level and probably in the lowest vibrational energy level also. Transitions from the ground state to any of the vibrational levels of the first excited state are allowed by spectroscopic selection rules and hence the spectrum exhibits a series of closely spaced lines, the intensities varying with the respective transition probabilities. Each line in turn may be resolved on either side of it into even more closely spaced lines representing transitions between rotational energy levels within each vibrational level. The electronic absorption spectrum of a

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Supercritical fluid chromatographic instrument is similar to the HPLC unit described earlier but incorporates two additional components, namely, a thermostatic column oven for precise control of temperature and a device to regulate the back-pressure called restrictor placed at the exit end of the column before the detector as shown in the Figure 10.42.

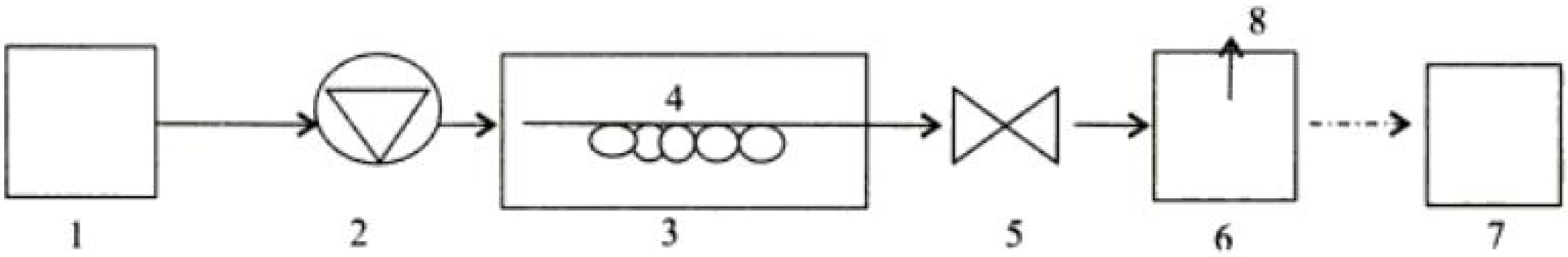

Fig. 10.42 Block diagram of instrument for supercritical fluid chromatography 1. solvent reservoir 2. microprocessor controlled syringe pump 3. oven 4. column 5. restrictor 6. detector 7. display 8. vent

The restrictor maintains the pressure in the column at the required level while facilitating the conversion of the mobile phase from the supercritical fluid to a gas phase before it reaches the detector.

Stationary phases used in supercritical fluid chromatography are similar to those used in liquid chromatography derived from bonded and cross-linked siloxanes.

The mobile phase used in supercritical fluid chromatography provides for the transport of solute molecules (similar to the role of the carrier gas in gas chromatography) and also interacts with the solute molecules influencing the selectivity factor. The solvent power of a supercritical fluid is highly dependent on its density, which in turn depends on the pressure and temperature. In general the solvent power of a supercritical fluid increases with increasing density at constant temperature and at constant density it increases with increasing temperature. The selectivity factor can thus be varied in supercritical fluid chromatography unlike in gas chromatography. The mobile phase most commonly used in supercritical fluid chromatography is carbon dioxide because of its advantageous features such as dissolving capability of a wide variety of non-polar organic substances, transparency to ultra violet light, absence of odour or colour and non toxicity besides its low cost. Organic modifiers such as methanol (~1%) may be added to carbon dioxide for analysis of polar organic substances.

Detectors for supercritical fluid chromatography are the same as those used in gas chromatography or HPLC. Flame ionisation detector is the most widely used detector. Ultraviolet and infrared spectral, fluorescence emission, flame photometric, thermionic and mass spectral detectors are also used.

Supercritical fluid chromatography finds use in the analysis of foods, drugs, pesticides, surfactants, polymers, fuels, explosives and propellants.

10.7.6 Planar chromatographic techniques

Planar chromatographic techniques includes the thin layer chromatography and paper chromatography.

Thin layer chromatography (TLC) makes use of a glass plate or aluminum foil as the support for the stationary phase. The support plate is coated with fine particles of an adsorbent such as alumina or silica gel as a thin layer of about 0.2 mm thickness and constitutes the chromatographic matrix for the separation of components of a mixture. The separation mechanism is primarily adsorption and partition may be involved depending on the amount of water immobilized during preparation of the TLC plate. The solute components get separated due to their different migration rates.

be easily controlled to suit the requirements of variation of temperature, length of flame and change in atmosphere (oxidising or reducing). Gaseous fuels can be preheated from hot waste gases and thereby enhancing the economic recovery of heat. They also find use in internal combustion engines. The disadvantages of gaseous fuels include their high cost of production and high risk of fire hazard.

11.5 Characteristics of a Good Fuel

Ideally a good fuel should have the following characteristics:

(i) *High calorific value*

(ii) *Moderate ignition temperature:* Ignition temperature is the lowest temperature to which the fuel must be heated for spontaneous smooth burning. A moderate ignition temperature is essential as a low ignition temperature can cause fire hazard during handling, storing and transporting while a high ignition temperature causes difficulty in igniting and burning the fuel.

(iii) *Low moisture content:* Moisture content decreases the calorific value of the fuel and also contributes to the cost of the fuel as well the cost of handling, storing and transporting the fuel.

(iv) *Low ash content:* Ash is the non-combustible waste material obtained by burning coal, which decreases the heating value of the fuel and poses disposal problem. Ash forms clinkers hindering complete burning of the fuel. Ash also contributes to the cost of the fuel by way of adding to the cost of handling and transporting the fuel.

(v) *Optimum combustion characteristics:* The fuel should burn in air without producing too much of smoke. It should not undergo spontaneous combustion causing fire hazard. The rate of combustion should be moderate to achieve the desired temperature quickly as a low rate will not produce the required higher temperature. The combustion process should be easily controllable to start or stop depending on requirement.

(vi) *Harmless combustion products:* The combustion products liberated on burning the fuel should be harmless from health and environmental pollution points of view.

(vii) *Caloric intensity:* Caloric intensity should be high for a fuel so that it produces a small flame and the heat liberated by combustion is concentrated over relatively a small area and high local temperature is attained. When the fuel has appreciable volatile matter content (particularly in the case of coal) it gives rise to a large flame spread over a larger area and hence the caloric intensity and local bed temperature are considerably less.

(viii) *Economical:* The fuel should be readily available, economical, easy to store and transport.

11.6 Calorific Value

The energy, mainly in the form of thermal or heat energy, released by the burning fuel is expressed in terms of calorific value. Calorific value of a fuel is defined as the total quantity of heat liberated by burning a unit mass or volume of fuel completely. The calorific value is expressed in units of calories per gram, one calorie being the amount of heat required to raise the temperature of 1 gram of water through 1° C at 15° C. A larger unit is kilo calorie per kilogram (k.cal/kg). In the case of gaseous fuels the unit is kilo calorie per meter cube (k.cal/m^3). The calorific value of a fuel is also expressed in terms British thermal unit (Btu) or centrigrade heat unit (chu). The equivalent value of 1 k.cal/kg is 1.8 Btu/lb and 1 Btu/lb = 0.55 cal/g.

The calorific value of a fuel can be experimentally determined. All fuels invariably contain some amount of hydrogen, which gets converted to steam and condenses to water at room temperature in a

Table 11.1 Ranking of coal and composition (Dry ash free basis)

Rank of coal	*Percentage (dry, ash-free basis)*					*Moisture content of air dried sample (%)*	*Calorific value k.cal/kg*
	C	H	O	N	VM		
Peat	45–60	4–7	20–45	0.7–3	65–70	25	4100–5400
Lignite	60–70	4–7	17–35	0.7–2.5	50–55	20	6500–7000
Sub bituminous coal	70–77	4–6.5	17–30	0.7–2.5	45–50	11	7000–7500
Bituminous coal	80–83	4–5.5	15–25	0.7–2	20–45	4	8000–8500
Semi-bituminous coal	85–90	4–5	15–20	0.7–2	9–20	1	8600–8800
Anthracite	92–95	3–4	2–3	0.5–2	3–7	1.5	8500–8600

11.8 Beneficiation, Cleaning and Storage of Coal

Coal mined in collieries is associated with clay or soil, mineral matter and dust. Coal with a specific gravity of 1.65 is separated from dense mineral contaminants by gravity separation of froth flotation using calcium chloride solution. The separated coal floating out is removed and is subjected to jig washing in which coal and the mineral matter are stratified in upper and bottom layers respectively by periodic upward and downward flow of water. The separated clean coal is stored taking care to avoid spontaneous combustion leading to fire hazard. However long term storage is avoided as it leads decrease in calorific value due to oxidation, deterioration of caking power and coking properties, increase in quantity of fines and fire hazard due to spontaneous combustion.

11.9 Analysis of Coal

The composition of coal varies with source and age of the coal and hence conventional chemical characterisation is not useful. Consumer oriented tests to assess the quality and fuel value have been evolved and prescribed by various standards such as British Standards, American Society for Testing and Materials (ASTM) or Indian Standards (IS). The quality of coal is assessed by two types of analyses: (a) *proximate analysis* and (b) *ultimate analysis*. The analyses are carried out as per prescribed procedures outlined below.

11.9.1 Proximate analysis

In proximate analysis contents of the moisture, volatile matter and ash are experimentally determined and the fixed carbon content is calculated. Proximate analysis of coal together with data on the calorific value and sulphur content is useful to assess the fuel value of coal and also to compare with coals of different sources or age.

Each chamber has provision to feed coal from the top, remove the coke formed from the bottom and also a gas outlet for the volatile matter formed during carbonization. Finely crushed coal is charged into the chambers and heated in the absence of air. The chambers are heated to about 1100–1200° C externally by burning a mixture of fuel gas such as producer gas and air in the flues. The hot gases from the flues pass on their sensible heat to one of the two sets of checker brickwork before escaping through chimney. After some time when the temperature of the first set of checker brick work is about 1000° C, the flow of the hot flue gases is changed to pass over the second set of checker brick work while a mixture of fuel gas and air used for burning in the flues is preheated by passing over the hot first set of checker brick work. The flow of the incoming fuel gas and the hot flue gases are alternated between the two sets of checker brickwork to recover sensible heat. During the heating of coal in the chambers, moisture is expelled first followed by the decomposition of coal in the temperature range of 300–450° C. The coal becomes plastic at about 500° C and transforms into black semi-coke at about 600° C. As the temperature of the chamber increases beyond 600° C the semi-coke decomposes giving off volatile matter and is finally transformed into steel grey hard coke. The process of carbonization progresses from the sidewalls of the chamber to the center and continues till the evolution of volatile matter completely ceases which may take about 12–18 hours. The yield of coke is about 70% of the coal charged.

The red hot coke formed at the end of carbonization is discharged from the chambers into coke cars and cooled either by wet or dry quenching. In wet quenching cooling water is sprayed on the coke. Wet quenching has several disadvantages such as the loss of sensible heat of coke, generation of large quantities of steam containing corrosive gases, and dirty water, which causes damage to equipment and pollution. In addition wet quenching also generates substantial amount of coke breeze or dust. In contrast dry quenching has several advantages such as recovery of sensible heat and the coke formed is dense, strong and graphitized. It is relatively dust free and dry. In dry quenching the red-hot coke discharged from the oven is transported to a brick chamber and cooled by passing inert gas such as nitrogen or sometimes air. The heated gas is utilised for recovering the sensible heat by circulating through boilers. The coke obtained by the Otto Hoffman method is non-reactive and amenable for use in metallurgical operations.

The volatile matter evolved during the carbonization process known as coke oven gas contains valuable products such as ammonia, hydrocarbons, tar and sulphur which are recovered in stages by passing through a series of towers. (i) *Recovery of tar*: The gas from the oven is passed upward through a tower in which liquor ammonia is sprayed to collect the tar and dust in a tank at the bottom of the tower. Tar is separated and ammonia is liberated by heating the collected liquid through steam coils for recycling. (ii) *Recovery of ammonia*: Ammonia present in the coke oven gas is recovered by passing the gas through a tower and spraying water or sometimes dilute sulphuric acid. Ammonia gas dissolves in water or forms soluble ammonium sulphate and is collected in a tank. (iii) *Recovery of naphthalene*: The coke oven gas after the recovery of ammonia is passed through yet another tower and sprayed with cold water to condense naphthalene. (iv) *Recovery of benzene and its homologues*: In the next stage the gas is sprayed with petroleum as it passes through a tower to recover benzene and other hydrocarbons present in the coke oven gas. (v) *Recovery of sulphur*: The coke oven gas contains substantial amount of sulphur in the form of hydrogen sulphide which is recovered by passing the gas through a purifying chamber packed with moist ferric oxide (Fe_2O_3) which forms Fe_2S_3. The iron sulphide formed is heated in air to recover sulphur in the form of sulphur dioxide and to regenerate ferric oxide. (vi) *Recovery of fuel gas*: The coke oven gas after the removal of the above mentioned valuable by products is finally collected in a gas holder for further use as it has a calorific value of about 5000 k.cal/m^3.

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cement. The hardened supersulphated cement cannot react further with sulphate as no free lime is available. Hence supersulphated cement structures resist the attack by sulphate as long as free lime is not available.

High alumina cement is manufactured from a mixture of bauxite with low silica content with an appreciable amount of iron containing bauxite (ferruginous bauxite) and limestone in suitable proportions. The mix is fused give high alumina cement corresponding to the formula $CaO.Al_2O_3 + 2.CaO.SiO_2$. The fused mixture is cooled and ground to a fine powder. The cement contains approximately equal proportions of alumina and lime, about 20% iron oxide and 4–7% silica. The predominant phase is CA along with a small amount of C_2S. The iron exists as C_2A-C_2F with other oxides in a solid solution. High alumina cement undergoes rapid setting and hardening attaining very high strength within 24 hours. It has a very high resistance to attack by sulphate solutions as well as sea water. The high resistance is attributed to the absence of free calcium hydroxide in the set cement. In the absence of free calcium hydroxide the possibility of formation of calcium sulphoaluminate with its accompanied huge volume expansion is negligible within the cement structure and hence no expansion cracking occurs. High alumina cement also finds use in the manufacture of refractory concrete suitable for furnaces and kilns.

12.5.5. Admixtures for concrete

Chemical admixtures are substances added to improve the properties of concrete. Admixtures include air entraining agents, water proofing agents, setting accelerators and water decreasing agents. *Air entraining agents* are surfactants such as oleic acid, caprylic acid, p-dodecyl benzenesulphonic acid, etc. They form microscopic air bubbles when added to gauging water of a concrete mix. The air bubbles are uniformly dispersed throughout the mix and get attached to the hydrophobic portions of the surfactant molecules. Concrete with its porous structure retains water in the capillaries and pores. The water within the capillaries freezes during winter resulting in volume expansion which in turn leads to spalling and cracking of the concrete. Concrete using air entraining agents resists spalling and cracking as the air bubbles offset the expansion cracking of the concrete. Concrete with air entrainers also has a better resistance to sulphate bearing waters and also provides better protection to the reinforcement.

Water decreasing agents decrease the water to cement ratio from the normal 0.3–0.5 by about 10–20% without affecting the setting and other engineering properties of the cement and concrete. Examples of water decreasing agents include lignosulphonate, melamine formaldehyde resin sulphonates, etc. The plasticity of the cement paste improves by the use of these agents as they react with the early hydration products of C_3A and C_2S phases reducing the inter-particle friction in the paste.

Setting accelerators such as calcium chloride and calcium formate accelerate the hydration of the C_2S and C_3S phases (contributing to the strength of the cement) and retard the hydration of C_3A. The optimum amount of calcium chloride is about 1.5% by weight and any excess promotes corrosion of the reinforcing steel.

12.6 Ceramics

Ceramics (Gk. *Keramos* = burnt matter) consist of a combination of non-metallic substances mostly silicates and metal oxides. The chemical combination of different metallic and non-metallic elements gives rise to ceramic materials with a variety of properties. The term ceramic is used to include structural clay products such as bricks and tiles, glass, abrasives, refractories, etc., which are mostly produced from naturally occurring minerals of silica and alumina. Highly refractory carbides, borides, nitrides,

against stretching (tension force) but is easily crumpled. The composite brick consisting of pieces of straw embedded in a block of mud on drying exhibits both compressive and tensile strength and hence makes a good building material. Another well known example of a composite is concrete consisting of aggregate (small stones or gravel) bound by cement. Concrete has good strength under compression and its strength under tension can be improved by embedding metal rods, wires, mesh or cables in the composite making it reinforced concrete.

12.11.1 Definition

Composites or composite materials are formed by combining two or more materials having different physical and chemical properties. The constituents remain separate and distinct within the finished structure but at the same time work together to give the composite unique properties that cannot be achieved by any of the components alone. The different constituents do not dissolve or blend into each other.

Composites are thus engineered materials which can satisfy the requirements of modern technology as they have several advantageous features such as high specific strength (ratio of tensile strength to density), high specific modulus (ratio of modulus of elasticity to density) and other desired properties. Further, these properties can be tailored to suit specific requirements by proper material selection.

Naturally occurring wood and bone are not considered as composites in a strict sense of the term. Wood consists of strong and flexible fibers of cellulose held together by lignin, the combination of cellulose and lignin giving wood its greater strength compared to a mere bundle of cellulose fibers as found in cotton. Similarly bone is a composite of the hard and brittle mineral hydroxyapatite, and the soft but strong protein collagen.

12.11.2 Constituents of a composite

A composite consists of a minimum of two phases, a bulk or continuous phase called the *matrix* and a dispersed phase called the *reinforcement*. The *matrix* material surrounds the individual reinforcing elements thereby protecting them against surface damage by mechanical abrasion or corrosion by environment. The matrix also supports the reinforcement materials by maintaining their relative positions. The matrix by virtue of its plasticity or ductility prevents the propagation of brittle cracks between individual reinforcing elements. Any externally applied stress is transmitted by the matrix to the dispersed phase. The matrix material should have good adhesive properties to bind the reinforcing elements because the ultimate strength of the composite depends to a large extent on the bonding strength of the matrix. Thermoplastic and thermosetting polymers, metals, carbon and ceramics are the most commonly used matrix materials.

The *reinforcement* imparts special mechanical and electrical properties to enhance the matrix properties. The composite exhibits material properties as determined by the properties of the constituent phases, their relative amounts and the geometry (size and shape) of the dispersed phase. A synergistic interaction between the phases produces material properties usually unavailable in naturally occurring materials. Examples of commonly used reinforcing elements include particulates such as gravel, carbon, ceramics, etc, rods and wire mesh of metals and fibers of glass and carbon.

If the composite is designed and fabricated properly, it combines the strength of the reinforcement with the toughness of the matrix. Composites also have the advantage of being amenable to tailor the properties such as strength and stiffness, by changing the amount or orientation of the reinforcement material.

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of elasticity compared to continuous fiber composites but the mechanical properties are isotropic and hence useful in the fabrication of components subjected multi-directional stresses. In addition the short fiber composites have the advantages of lower cost of production compared to continuous fiber aligned composites, rapid rate of production as well as forming intricate shapes by the use of fabrication techniques such as injection moulding, compression moulding and extrusion.

12.11.7 Structural composites

These are broadly classified into two types (i) laminar composites or laminates and (ii) sandwich panels. The properties of these composites depend on the constituent materials as well as on their geometry.

Laminar composites consist of stacks of sheets or panels made of cotton fabric, paper, or continuous and aligned glass fiber reinforced plastics, cemented together. The sheets are arranged so that the orientation of high strength of the sheets varies in successive layers. Laminates have a high strength in different directions in two dimensional planes.

Sandwich panels consist of a sandwich of an inner 'core' of relatively lower strength and stiffness such as rubber, polymer foams, balsa wood or inorganic cements covered by strong sheets or 'faces' made of plywood, fiber reinforced plastics or steel, aluminum alloys or titanium. The outer sheets bear in-plane loading as well as transverse stresses while the inner core provides resistance to deformation and also shear rigidity along the planes perpendicular to the faces. Sandwich panels containing honeycomb core made of foils interlocked into hexagonal cells with their axes oriented in a perpendicular direction to the planes of the faces are widely used. Sandwich panels are used in the construction of walls, building roofs and floors, aircraft wings, fuselage and tail plane skins.

12.11.8 Metal matrix composites (MMC)

Metal matrix composites have certain superior mechanical properties compared to other types of composites. MMCs have higher transverse strength and stiffness, greater shear and compressive strengths and better high temperature capabilities. In addition they have advantageous physical properties such as high electrical and thermal conductivities, non-flammability, resistance to most radiations and negligible moisture absorption.

Metal matrix composites are fabricated by a variety of methods such as (i) solid state, (ii) liquid state, (iii) deposition and (iv) in situ.

In the solid state methods *diffusion bonding* is adopted for matrix metals in the form of sheets or foils. The metal is brought into close contact with reinforcing material (fibers) by making a sandwich of the fiber mat between two sheets to form a ply. The ply is consolidated through a suitable combination of temperature and pressure to form the composite. MMCs of titanium, nickel, copper and aluminum reinforced with boron fibers are made by the diffusion bonding method. *Powder metallurgy* is yet another solid state method suited for the production of discontinuous fiber, whisker or particulate reinforced metals. The components are mixed and consolidated by the simultaneous application of high temperature and pressure. Multi-filamentary superconducting composites containing Nb_3Sn or V_3Ga in bronze matrix and silicon carbide whisker (single crystals) or particle reinforced aluminum matrix are mostly produced by powder metallurgy technique.

In the liquid state methods *melt stirring* is a simple method in which the reinforcement particles, whiskers or discontinuous fibers are mixed with the molten metal and cast in the conventional manner. *Compocasting* or *rheocasting* is a modified melt stirring method in which the molten metal is allowed to cool to a more viscous state for ease of stirring and efficient mixing and dispersion of the reinforcement

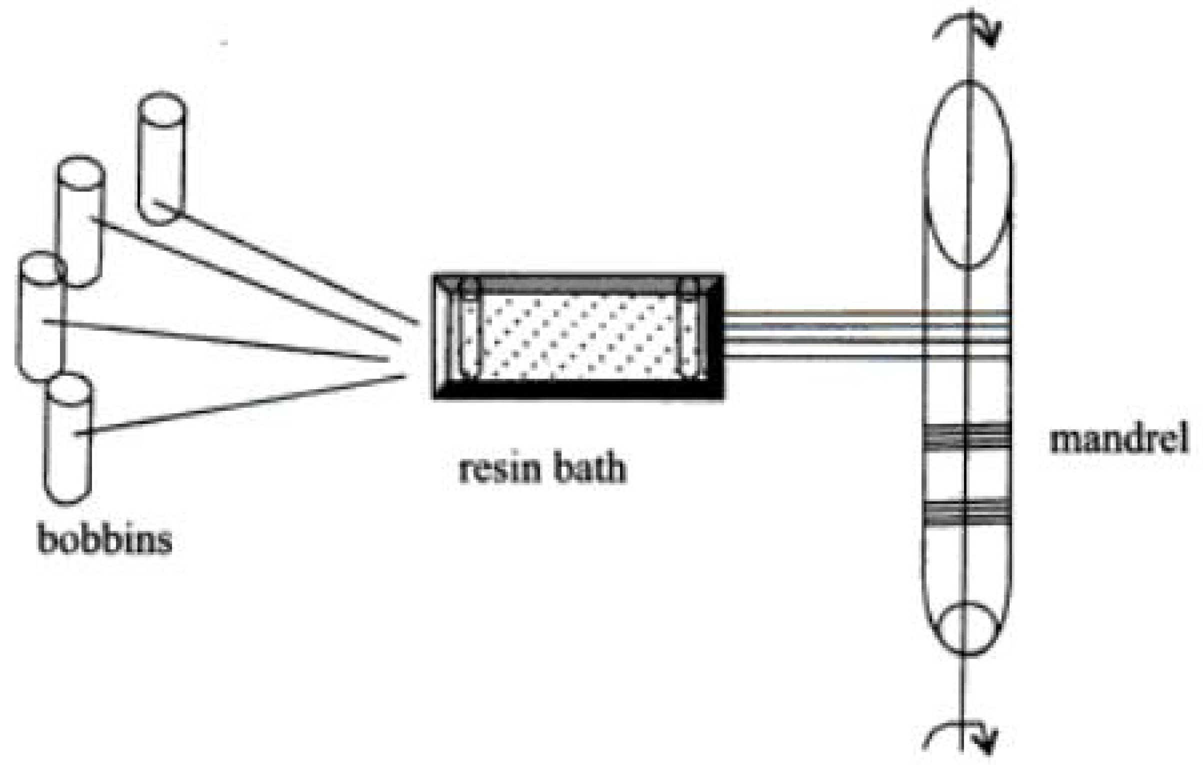

Fig. 12. 5 Filament winding operation

Prepeg is a continuous fiber (glass, carbon or aramid fibers) impregnated with a thermosetting resin commercially made available in the form of a tape which is moulded and cured into the desired component without adding any resin. Woven fibers are impregnated with a solution of the resin followed by the evaporation of the solvent in a drying tower. Unidirectional prepegs are commonly prepared by hot melt method in which bundles of fibers are passed through molten resin and sandwiched between carrier and release papers by heated calendaring rollers to form a sheet. Figure 12.6 shows a schematic diagram of the prepeg tape production.

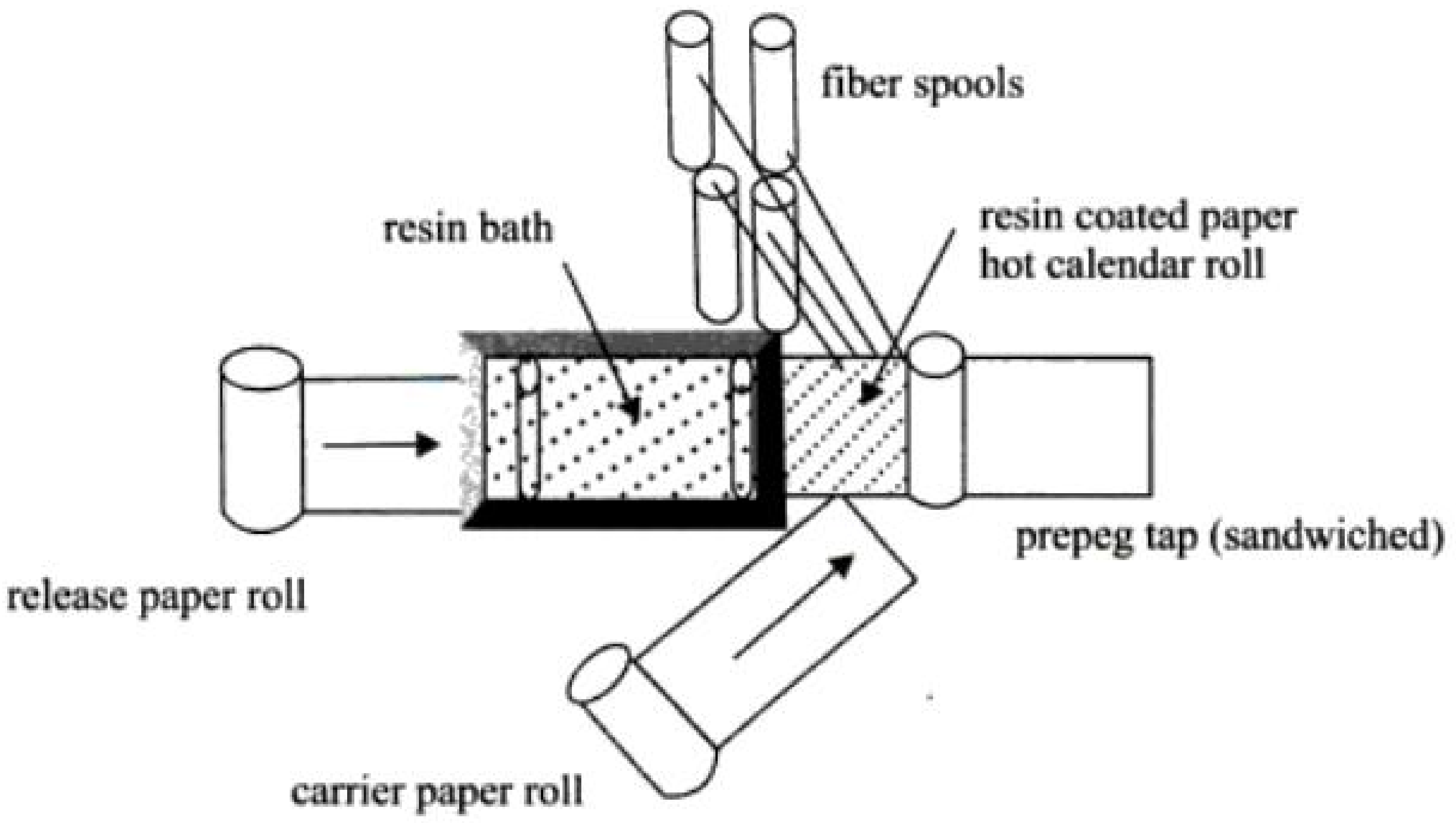

Fig. 12.6 Schematic diagram of prepeg tape production

Calendaring ensures uniform impregnation of the fibers by the resin coated release paper. The finished prepeg tape consisting of the partially cured resin embedding the aligned fibers is wound on cardboard spools for marketing. For fabricating the desired structural component the prepeg plies are laid up in desired orientation and thickness and the stack is cured by compression moulding or in an autoclave to form a composite laminate.

Fiber glass composites have good strength with service temperatures up to 200° C but do not possess stiffness and rigidity for high end applications. Fiber glass composites find use in the manufacture of storage tanks, pipes, automotive parts, marine bodies and as industrial flooring.

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12.16 Nanomaterials

The term 'nanomaterials' is used to describe the preparation and application of materials with at least one dimension in the nanometer (10^{-9} m) scale range. Nanoscience and nanotechnology are emerging areas of technological importance with profound impact on a variety of physical sciences, engineering, biology and medical fields. Nanoscience involves the study of materials at atomic, molecular and macromolecular level where the properties of materials differ significantly from those of bulk materials. For example, the electronic structures of metal and semiconductor crystals differ from those of isolated atoms and bulk materials. Even metals show non-metallic band gaps in the 1–2 nm sized nanocrystals as in the case of Hg clusters (the band gap decreasing with increasing cluster size). Similarly 1–2 nm sized nanometal particles of gold exhibit unusual catalytic activity. The unique properties of nanomaterials in general have been attributed to two important characteristics, namely, their large surface area and size effect or quantum effect, because of their small size.

Nanotechnology aims at exploiting the properties of nanomaterials which allow them to exhibit novel performance characteristics and involves fabrication of devices, structures and systems with industrial applications. Though the term 'nanotechnology' is of recent origin, the use of nanomaterials has been in vogue probably since as early as the fourth century A.D., during which period Roman glassmakers fabricated coloured articles of glass embedded with nanoparticles of silver and gold. Photography, another technological marvel which came into practice in the 18th century, is based on the latent image formed by nanoparticles of silver produced by light induced reduction of silver halides. Richard Feynman (Nobel laureate in physics in 1965) is credited for creating interest in the development of nanotechnology through his visionary and prophetic lecture entitled 'There is plenty of room at the bottom' at the American Physical Society meeting in 1960. He predicted the use of etching by a beam of electrons (electron-beam lithography) and nanoscale circuits in nanoelectronic devices and computers. He also recognized that biological systems have been making nanoscale functional devices since the beginning of life itself.

A few important chronological developments in the area of nanotechnology include (1) the fabrication of nanosized quantum wells in 1970s by thin film epitaxial growth techniques; (2) laser vapourization of metals to form condensed metal atom clusters, synthesis of fullerene (C_{60}), invention of scanning tunneling microscope (STM) and atomic force microscope (AFM) for viewing, characterizing and manipulation of nanostructures, fabrication of single electron transistor, development of electron-beam lithography, development of nanometer thick magnetic storage devices during 1980s; and (3) synthesis of carbon nanotubes, development of photonic crystals, molecular switches, field-effect transistors, etc. during 1990s.

Examples of such nanomaterials include (i) nanocrystals and clusters of metals, semiconductors (quantum dots) and magnetic materials; (ii) nanoparticles of ceramic oxides and two-dimensional arrays of metals, semiconductors and magnetic materials; (iii) nanowires and nanorods of metals and semiconductor oxides, nitrides and sulphides; (iv) nanotubes of carbon and layered metal chalcogenides; (v) nanoporous solids of zeolites, and phosphates; (vi) thin films and surfaces of a wide variety of materials, and (vii) superlattices of three-dimensional structures of metals, semiconductors and magnetic materials. Such materials have potential applications in materials technology, optoelectronics, nanoelectronics, information technology, medicine, etc. This section gives a brief introduction to the preparation and properties of nanomaterials and their potential applications.

12.16.1 General methods of synthesis of Nanomaterials

Two broad approaches have come into vogue for the preparation of nanomaterials. The 'top-down approach' involves mostly mechanical and electromechanical methods for cutting down the bulk materials

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C_h (*n*, *m*), if (*n*–*m*) is a multiple of 3, the tube is metallic, otherwise the tube is a semiconductor. Tubes with armchair structure (*n* = *m*) have been shown to be metallic while all other types are semiconductors. In the case of semiconducting chiral tubes, the band gap energy decreases with increasing diameter of the tube. The nanotubes function as one-dimensional *quantum wires* conducting along the axis of the tubes. Electron transport in a single metallic nanotube lying across two metal electrodes at 0.001K showed step-like features in the current-voltage diagram resembling that of a field effect transistor. Electron transport in the tube has been explained on the basis of electron tunneling through discrete states.

Metallic nanotubes have very high electrical conductivity estimated to be about a billion amperes/cm^2 (much higher than even copper wires). Copper wire melts due to resistive heating on passage of one million amperes/cm^2. The very high electrical conductivity of carbon nanotubes has been attributed to the negligible amount of defects (defects scatter electrons) and hence the CNTs have very low resistance. They also have high thermal conductivity, about a factor of 2 more than that of diamond.

Magnetoresistance refers to the phenomenon of change in the resistance of a material due to the application of a DC magnetic field. At low temperatures, carbon nanotubes show a negative magnetoresistance effect as the resistance decreases with increasing DC magnetic field, i.e., conductance increases. The increase in conductance is explained on the basis that more energy levels called Landau levels are created due to the spiraling motion of electrons about the magnetic field. These new energy levels lie very close to the highest filled energy level (Fermi level) and allow the electrons to acquire more energy.

Mechanical properties of carbon nanotubes are quite unique which have been attributed to sp^2 hybridized C–C bonds. CNTs are the stiffest and strongest materials in terms of elastic modulus and tensile strength. The stiffness or elastic flexibility of a material is expressed in terms of Young's modulus which is the rate of change of stress as a function of applied strain. The Young's modulus of carbon nanotubes is ~1000 GPa, about ten-times greater than that of steel. The larger the value of Young's modulus, the less flexible the material is. This implies that it is difficult to bend CNTs. However, it is not true as CNTs are so thin. They exhibit high resilience on bending and can be straightened back without any damage. Materials generally fracture on bending due to the presence of defects and grain boundaries. However CNTs have very few such structural defects in their walls and hence do not fracture on bending. In addition, the hexagonal carbon rings on the walls of CNTs change their structure during bending and do not break. This has been attributed to the sp^2 hybrid bonds which can undergo rehybridization by changing the *s-p* admixture on bending. The tensile strength is a measure of the amount of stress required to pull apart or break the material. The tensile strength of CNTs is about 60 GPa (about 20 times that of steel). CNTs are not as strong under compression. They undergo buckling under compressive, torsional or bending stress because of their hollow structure.

Vibrational properties of carbon nanotubes are expressed in terms of normal modes of vibration of carbon atoms in the tubes just as the normal modes of vibration exhibited by molecules. CNTs have two normal modes of vibration, (i) the A_{1g} mode involves an 'in and out' oscillation of the diameter of the tube with a frequency of 165 cm^{-1} and (ii) the E_{2g} mode which involves an oscillation between the sphere and an ellipse with a frequency of 17 cm^{-1}. The frequencies of these two modes of vibration are Raman-active. The frequency of A_{1g} mode varies with the radius of the tube and has been routinely used to determine the radius of the CNTs.

Thermal properties of CNTs are expected to be very good with high thermal conduction along the tube exhibiting a 'ballistic conduction' property but insulator characteristics lateral to the tube axis. Thermal conductivity is expected to be about 15–20 times that of copper (6000 W/(m.K) and

41. How do solid lubricants function?
42. Write a note on synthetic lubricants.
43. What is adhesive action? What factors influence adhesive action.
44. Classify the explosives. Give examples.
45. How is an explosive assessed?
46. What are rocket propellants? What are their characteristic features?\
47. How are carbon nanotubes synthesized?
48. Write a brief note on the applications of CNTs.
49. What are nanoparticles? What are their characteristic properties?
50. Explain the principle and working of SEM.
51. Give a brief account on scanning microscopic techniques.

13

CORROSION AND IT'S CONTROL

13.1 Introduction

Corrosion is a general term that refers to the deterioration and ultimate destruction of a metal due to its reaction with the surrounding gaseous or liquid environment. Corrosion is a decay process in which metals exhibit their natural tendency to revert to their native combined state of existence as minerals (e.g., oxides, sulphides, carbonates, etc.). Only metals such as gold and platinum exist in nature as metals and are not susceptible to corrosion under ordinary atmospheric conditions and hence are called noble metals. Most of the modern day industrial as well as domestic applications involves the use of metals and alloys and corrosion causes a heavy loss to industries in particular and impairs the economic status of a society in general. All metals and alloys are susceptible to corrosion under different environmental conditions. For instance, gold which has an excellent resistance to corrosion under atmospheric conditions gets quickly corroded when exposed to mercury at ambient temperature. On the other hand, iron gets rusted slowly in the atmosphere but is unaffected by mercury. Control of corrosion rather than its prevention will lead to effective engineering, because it is impracticable to eliminate corrosion.

13.2 Types of Corrosion

Corrosion may be broadly classified into two types based on the mechanism of corrosion. These include (i) dry corrosion or corrosion in gaseous environment, and (ii) wet corrosion.

13.3 Dry Corrosion

One of the most common ways by which metals get corroded is by direct interaction with atmospheric gases such as oxygen, hydrogen sulphide, halogens, sulphur dioxide, oxides of nitrogen and chemicals in close contact with the metal. Oxygen is primarily responsible for corrosion of most metallic structures as compared to other gases and chemicals.

Direct attack on metals by oxygen even at ambient temperatures in the absence of moisture leads to oxidation corrosion, that is, the formation of the corresponding metal oxide, which is normally a thermodynamically spontaneous process. The rates of oxidation of metals at ambient temperatures are low but at higher temperatures, oxidation is also kinetically favoured. Alkali metals (eg., sodium and potassium) and alkaline earth metals (e.g., magnesium and calcium) undergo oxidation even at low temperatures whereas at higher temperatures practically all metals except silver, gold and platinum are oxidized. The oxide film formed at ambient temperature is quite thin and generally not visible. However if the oxide film is formed at high temperatures it exhibits various tints of colours due to interference of light reflected at the lower and upper surfaces of the oxide film. The colours disappear as the thickness of the oxide film increases. Oxidation for prolonged periods at high temperatures results in the formation of a scale which may protect the surface against further corrosion at high temperatures and oxidizing environments. The scale formed ruptures after attaining a certain thickness, thereby exposing the fresh metal surface to further oxidation. Such scales do not offer any protection to the metal in a liquid environment.

13.3.1 Formation of oxide film

The oxidation of metals responsible for the formation of the scale is electrolytic in nature, and the electrical properties of the corrosion products determine the rate of oxidation. The oxidative corrosion may be considered to involve the reactions of oxidation of the divalent metal to form the metal ion with the simultaneous release of electrons and the combination of the electrons with oxygen to form oxide ions.

$$M \longrightarrow M^{2+} + 2\,e^- \tag{13.1}$$

$$\tfrac{1}{2}\,O_2 + 2\,e^- \longrightarrow O^{2-} \tag{13.2}$$

The overall reaction may be represented as

$$M + \tfrac{1}{2}\,O_2 \longrightarrow M^{2+}O^{2-} \text{ (metal oxide film)} \tag{13.3}$$

The formation of metal oxide film at the surface actually tends to restrict further oxidation. The electrical properties of the ions and the diffusion of oxygen are responsible for continued oxidation and growth of the film into an oxide scale. The growth of an oxide film can occur due to (i) migration of metal ions outwards to the surface, (ii) migration of oxide ions from the surface to the bulk, (iii) simultaneous migration of metal ions and oxide ions, and (iv) penetration of molecular oxygen through the metal-oxide interface. This migration of cations and anions is responsible for the ionic conduction of solids. In general, outward diffusion of metal ions and electrons is likely to be more rapid due to the fact that cations are smaller in size compared to the oxide ions.

13.3.2 Pilling and Bedworth rule

According to Pilling and Bedworth, the oxidation resistance of a metal is related to the specific or molar volume ratio of the corrosion product, namely, the metal oxide and the metal. It is expressed mathematically as

$$R = (M/D) \times (d/m) \tag{13.4}$$

Where M and m are the molecular weight and atomic weight of the metal oxide and the metal respectively, D and d are the densities of the oxide and the metal respectively. The ratio R indicates the volume of oxide formed from a unit volume of metal. If $R < 1$, the oxide layer can cover the metal surface only when it is under tension. However, such tension will tend to produce cracks thereby exposing the metal surface to oxygen. For instance, the volume ratio of CaO to Ca is 0.64 and hence the oxide cannot protect the metal from corrosion by oxygen. Other examples include alkali metals and magnesium with the value of R being less than one. On the other hand, if $R > 1$, as in the case of copper-oxygen system (the volume ratio of Cu_2O to Cu is 1.71) the oxide is able to cover the metal surface effectively. The strongly adherent non-porous oxide layer protects the metal from further oxidation. Other examples where $R > 1$ include aluminum, iron, nickel and zinc.

The above correlation is approximate only, since the same metal can follow different oxidation rates as a function of time or temperature. Metals having more than one oxidation state can form complex oxide films. Fox example, iron on heating to temperatures above 575° C, is covered with a scale consisting of a lower layer of FeO, a middle layer of Fe_3O_4 and a top layer of Fe_2O_3. At temperatures below 575° C, FeO is unstable and the scale consists of the other two layers. At still lower temperatures only Fe_2O_3 layer is formed. FeO decomposes readily to Fe and Fe_3O_4 in acids and hence its presence in the scale formed at higher temperatures makes descaling of iron easy by pickling in acids. The scales formed at lower temperatures are not easily removed.

13.3.3 Dry corrosion by other gases and chemicals

Other gases present in the working environment such as chlorine, fluorine, sulphur dioxide, hydrogen sulphide and oxides of nitrogen are also corrosive. The extent of corrosion of a particular metal depends on the chemical affinity of the metal towards the reactive gas. Hydrogen sulphide attacks metals forming the corresponding metal sulphide and releases atomic hydrogen. The atomic hydrogen diffuses readily into the metal and collects at the void spaces where it combines with atomic hydrogen to form hydrogen gas. The accumulation of the gas develops a high pressure causing cracks and blisters in the metal. The condition is known as ***hydrogen embrittlement***. At higher temperatures molecular hydrogen undergoes disassociation to yield atomic hydrogen. The atomic hydrogen on coming into contact with steel combines with the carbon of steel to form methane gas which collects in voids. As the pressure increases due to the accumulation of the gas cracks occur in steel, a condition known as ***decarburisation***. The corrosion product may form a porous or non-porous film. For example, chlorine attacks tin and forms the volatile $SnCl_4$ and hence, the metal is continuously exposed to the corrosive gas and corrosion proceeds rapidly. In contrast a non-porous protective film of AgCl is formed on silver and decreases the rate of further corrosion. Sulphur dioxide, hydrogen sulphide and the oxides of nitrogen are acidic in nature and attack most metals. The liquid metal mercury dissolves most metals by forming amalgams thereby corroding them.

13.4 Wet Corrosion

The corrosion of metal in aqueous environments is more prevalent than under dry conditions. Iron undergoes corrosion to form rust (hydrated ferric oxide, lepidocrocite) and renders the metal useless as a structural material. The rust formed on the surface of iron is loose and does not adhere to the metal surface. Besides it absorbs moisture and hence offers little protection to the metal. Iron does not corrode in dry air or in water that is completely free from oxygen. Thus both oxygen and water are essential for rusting. Corrosion in the form of rust is accelerated by the presence of rust itself as well as acids and electrolytes. Iron in contact with a less-reactive (or relatively more noble) metal like copper also accelerates the formation of rust.

13.4.1 Electrochemical theory of corrosion

According to the electrochemical theory of corrosion, wet corrosion is a two step process which occurs simultaneously, namely, oxidation and reduction. The surface of a piece of iron in contact with an aqueous solution of electrolyte becomes a galvanic or a voltaic cell consisting of anodic and cathodic regions. The iron is oxidized to ferrous iron (Fe^{2+}) and the ions leave the metal lattice and pass into the solution. The electrons released during the oxidation migrate to the cathodic region through the metal lattice connecting the two regions. The circuit is completed by the migration of ions through the aqueous solution of the electrolyte in contact with the metal. The galvanic cell formed facilitates the flow of positive current from the anodic region to the cathodic region through the electrolyte leading to the dissolution or corrosion of the anodic region. The anodic oxidation may be represented as

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \qquad (13.5)$$

The electrons are utilised at the cathodic region either to form hydrogen or hydroxide ion depending on the pH of the medium. In an acidic medium hydrogen is liberated.

$$H^+ + e^- \longrightarrow H \text{ and } H + H \longrightarrow H_2 \tag{13.6}$$

In neutral or a weakly alkaline medium, hydroxide ions are formed by the reduction of absorbed oxygen

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^- \tag{13.7}$$

The overall reaction occurring at the anodic and the cathodic regions in acid medium leading to the formation of rust may be represented as

$$4\,Fe + 3\,O_2 + 6\,H_2O \longrightarrow 2\,(Fe_2O_3.3\,H_2O) \tag{13.8}$$

If corrosion is accompanied by hydrogen evolution, the reaction may be represented as

$$4\,Fe + O_2 + 10\,H_2O \longrightarrow 2\,(Fe_2O_3.3\,H_2O) + 4\,H_2 \tag{13.9}$$

In neutral or weakly alkaline medium the sequence of reactions may be given as

$$4\,Fe \longrightarrow 4\,Fe^{2+} + 8\,e^- \text{(at the anodic region)} \tag{13.10}$$

$$2\,O_2 + 4\,H_2O + 8\,e^- \longrightarrow 8\,OH^- \tag{13.11}$$

$$4\,Fe^{2+} + 8\,OH^- \longrightarrow 4\,Fe(OH)_2 \qquad \text{(at the cathodic region)} \tag{13.12}$$

$$4\,Fe(OH)_2 + 2\,H_2O + O_2 \longrightarrow 2\,(Fe_2O_3.3\,H_2O) \tag{13.13}$$

Though corrosion of iron occurs in the anodic region the rust is formed at the cathodic region due to the fact that the smaller Fe^{2+} diffuses rapidly towards the cathode to combine with the OH^- ions formed near the cathode and the combination results in the deposition of rust near the cathodic region.

13.4.2 Formation of anodic and cathodic regions and Types of Wet corrosion

The formation of anodic and cathodic regions on the surface of a metal may be attributed to factors such as (i) presence of impurities in the metal, (ii) differences in oxygen concentration, and (iii) cracks in the surface film and roughness of the metal surface.

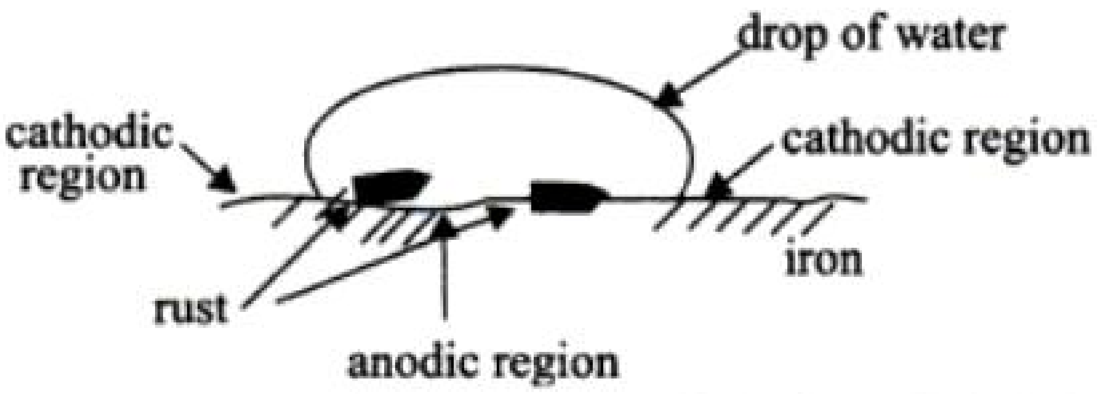
(i) Presence of impurities

The presence of impurities such as iron, lead or carbon in zinc results in the setting up of galvanic cells leading to anodic corrosion of zinc. A similar feature is observed in water distribution systems consisting of a combination of copper and iron pipes. Such corrosion is also called ***differential metal corrosion*** or ***galvanic corrosion***. In general when two different metals are in electrical contact in the presence of an electrolyte, the metal higher up in the electrochemical (galvanic) series becomes anodic and suffers corrosion because of its higher oxidation potential (natural tendency to undergo oxidation). Examples of differential metal corrosion include plain carbon steel (anode) in contact with stainless steel and brass. Screws, bolts and nuts on plain carbon steel should be of more noble material such as Cr-Ni steel. Brass, an alloy of copper and zinc (anode), in contact with an aqueous solution undergoes dezincification leaving behind porous copper metal mass. Addition of a small quantity of arsenic, antimony or phosphorous makes brass resistant to dezincification. Cast iron in contact with water or soil is transformed into rust, which together with flakes of graphite forms a spongy mass. This type of corrosion is called ***graphitic corrosion***. The galvanic corrosion may be avoided by a proper selection of metals and alloys based on their position in galvanic series.

(ii) Differences in oxygen concentration on the surface

As a result of uneven exposure to atmospheric oxygen a metal surface in contact with an aqueous solution can get corroded easily. This is due to the formation of galvanic cells or more specifically electrolyte concentration cells. The parts of the metal exposed to a higher concentration of oxygen become cathodic while parts of the metal exposed to a relatively lower concentration of oxygen become anodic and get corroded. Such corrosion is referred to as ***differential aeration corrosion***. Examples of this type of corrosion include drop corrosion, crevice corrosion, deposit corrosion and water line attack.

Drop Corrosion, is a form of differential aeration corrosion observed when a drop of an electrolyte solution placed on a metal creates a differential aeration cell as shown in the Figure 13.1.



at the cathode:

$$\frac{1}{2}O_2 + 2e^- + 2H_2O \longrightarrow 2OH^-$$

at the anode:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Fig. 13.1 Differential aeration resulting in drop corrosion

This is due to the fact that the dissolved oxygen concentration decreases in the drop as it is consumed by the cathodic reaction. Oxygen from the surrounding atmosphere diffuses in, to replenish the solution but diffusion occurs more readily at the periphery of the drop rather than at the center. Thus the peripheral regions of the drop become oxygen rich and the metal in contact acts as cathodic region while the metal just below the center of the drop acts as an anodic region. Corrosion occurs at the oxygen deficient region (anodic) directly beneath the center of the drop and ring of rust develops around the center.

Crevice corrosion is formed between different metallic objects or between a metal and a non-metallic material joined by bolt, nuts, rivets and washers. The crevice on coming into contact with a liquid becomes anodic region as the oxygen supply to this area is less compared to other parts and gets corroded preferentially (Figure 13.2).

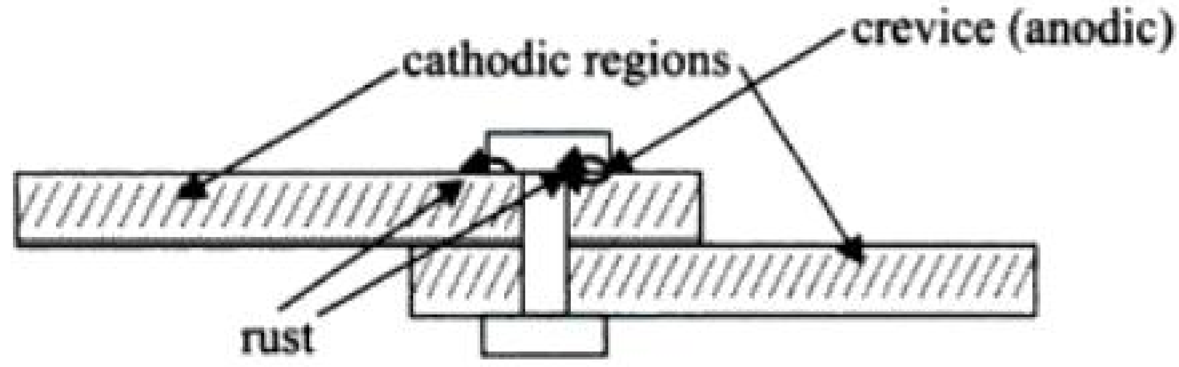


Fig. 13.2 Crevice corrosion

Deposit corrosion is a form of differential aeration corrosion occurring when metallic objects in contact with water are partially hidden by dirt, debris, sand, etc., thereby inhibiting access to air to replenish the dissolved oxygen. The areas underneath the covered portion become anodic and get corroded once again due to the setting up of a differential aeration cell.

Water line corrosion occurs when a metal is partly submerged in water. The part of the metal near the waterline is well aerated and acts as a cathode. Areas of the metal, deep inside the water become anodic as they are exposed to lower concentrations of oxygen. Corrosion occurs in the anodic region and simultaneously reduction of oxygen to hydroxide ion occurs at the cathodic region. The ferrous iron and hydroxide ions interact to ferrous hydroxide at a region in between the anodic and cathodic regions. The ferrous hydroxide is oxidized to rust by the dissolved oxygen from the surrounding water. The process of corrosion progresses as the anodic region shifts upwards slowly until the whole of the specimen is corroded (Figure 13.3).

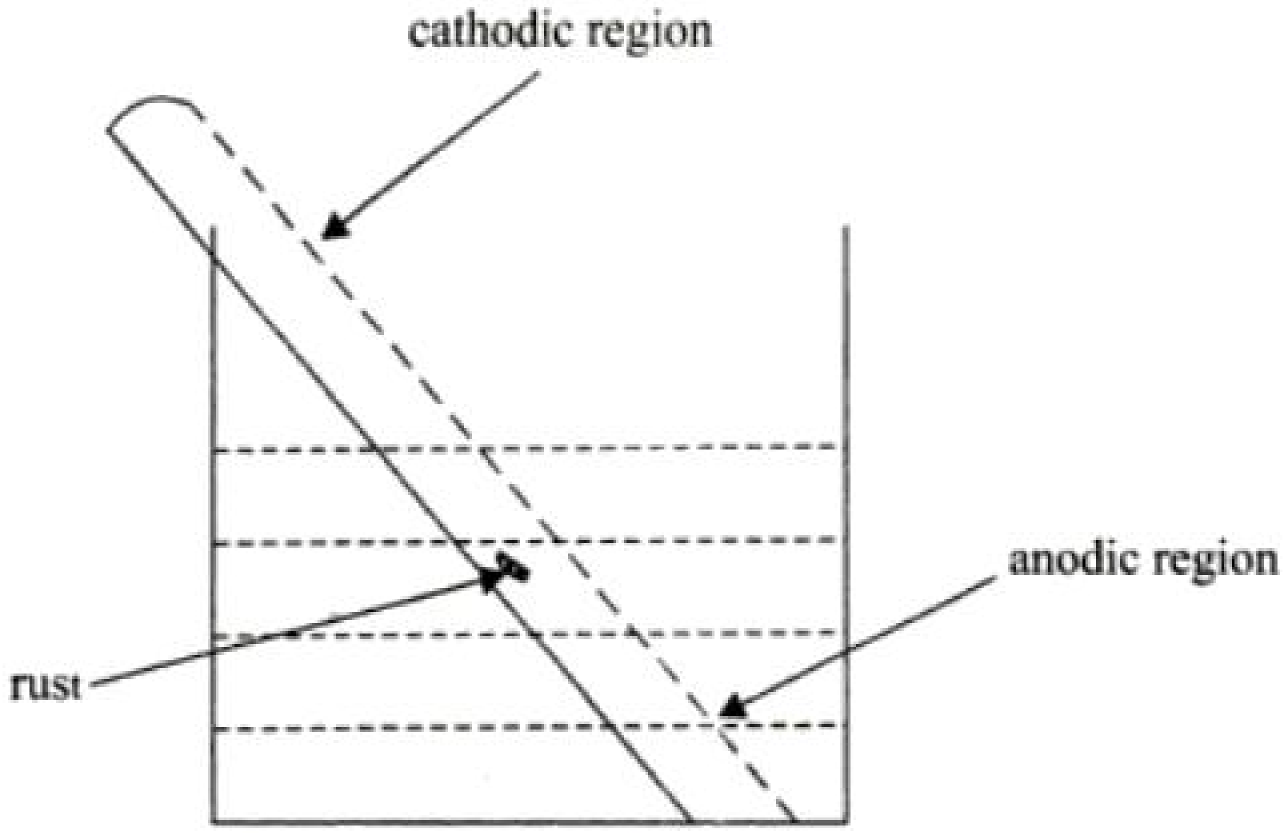


Fig. 13.3 Water line corrosion

(iii) Cracks in the surface film and roughness of the metal surface

Metals such as iron and zinc form oxide films readily on exposure to air. The oxide film may be porous or thin or cracked at certain points on the surface. It is easier for the metal atoms to leave the lattice at these weak points than at those points when the oxide film is more perfect. When the metal is in contact with an electrolyte, anodic areas develop at the points where the oxide film is cracked or weak and cathodic regions occur at points where the oxide film is intact. Corrosion on such an imperfectly covered metal surface is shown in the Figure 13.4.

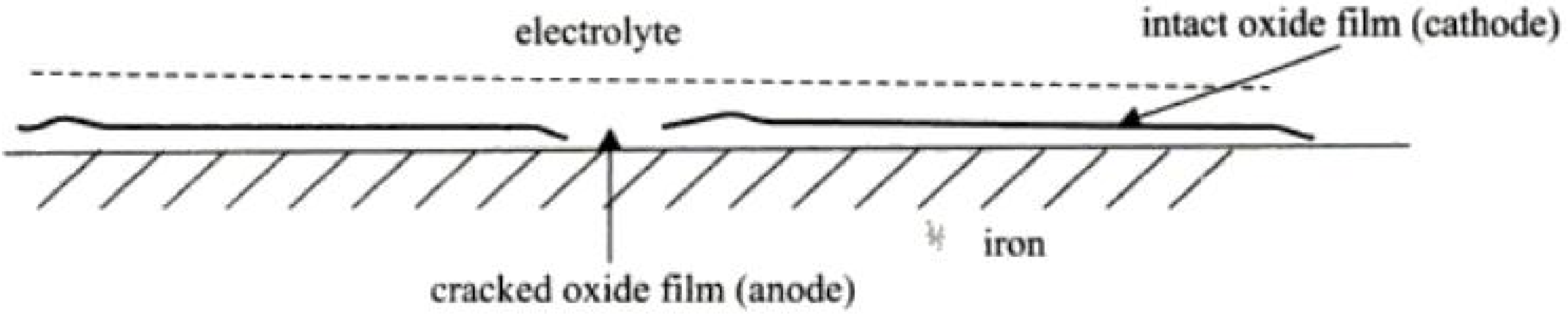


Fig. 13.4. Corrosion at cracks in surface film

Pitting is a localised form of corrosion resulting in the formation of pinholes or pits. A pit is initiated on certain defective sites on the oxide film due to cracking of the protective film at specific points. Adsorption of activating species such as chloride ions induces oxidation of the metal underneath the pit to ferrous iron. The combination of a large cathode and a small anode leads to severe corrosion of the anode and the local excess of metal ions generated in this area attracts the chloride ions. The hydrolysis of the metal ions leads to the formation of an acidic solution, which also functions as a strong electrolyte. The ferrous iron and the hydroxide ions interact forming ferrous hydroxide in the pit, which gets oxidized to rust. The rust covers the bottom of the pit and screens it from oxygen leading to a severe highly localised corrosion (Figure 13.5).

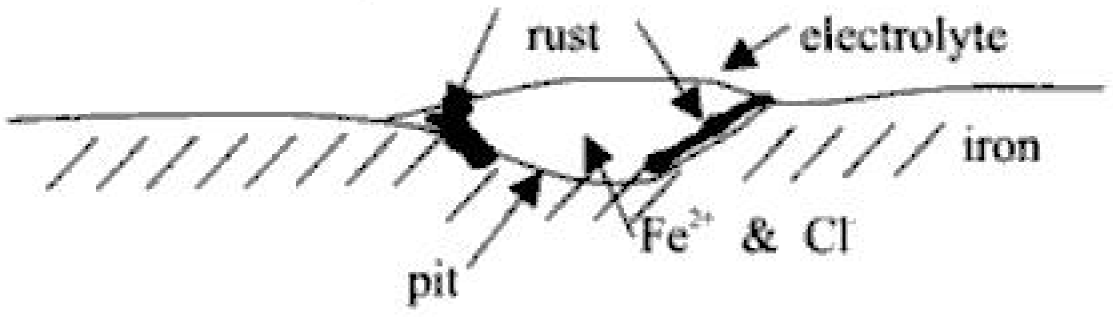


Fig. 13.5 Pitting

13.5 Atmospheric Corrosion

In normal atmospheric conditions corrosion occurs as a result of the joint action of two factors, namely, oxygen and moisture. If either of these factors is missing, corrosion does not occur. Thus iron exposed to atmosphere with a relative humidity of greater than 60% undergoes corrosion rapidly. Steel covered with ice does not rust because water in the form of liquid is required to initiate and propagate corrosion. The presence of acidic gases such as sulphur dioxide and common pollutants such as soot, dust particles and solid particles of ammonium sulphate in air increase atmospheric corrosion. Rain provides the moisture necessary for atmospheric corrosion. In addition, it may wash off any protective oxide film thereby exposing the metal to corrosion particularly in the case of iron and chromium. Oxygen can function both as a corrosion inhibitor and as a stimulator. Oxygen forms a protective oxide film on aluminium, nickel and stainless steel thereby preventing atmospheric corrosion. On the other hand oxygen also promotes corrosion by getting reduced to hydroxide ions at the cathodic regions. Hence deaeration of aqueous solutions is an excellent method of reducing corrosion particularly in boilers.

13.6 Soil Corrosion

This type of electrochemical corrosion is of particular importance in submerged structures. The various factors responsible for soil corrosion include acidity of the soil, moisture content, mineral content, types of microorganisms present, and organic matter content. In highly acidic soils metals undergo corrosion accompanied by liberation of hydrogen. In neutral and mildly alkaline soils, the mineral content and moisture content of the soil have a major role in influencing the rate of corrosion. Soils with a high moisture and mineral content also have high electrical conductivity and promote corrosion. Sandy and gravel containing soils are porous and well aerated, once again creating differences in oxygen concentration at different places on the submerged metal surface. Organic matter may form soluble complexes with metals thereby facilitating corrosion. Aerobic and anaerobic microorganisms also induce corrosion by consuming oxygen or depositing slime causing differential aeration corrosion.

13.7 Stress Corrosion and Stress Cracking

Even in pure metals and alloys, the regions under stress due to heavy working such as rolling or drawing become anodic and undergo corrosion. Stress corrosion leading to cracking has been observed in several alloys such as nickel brasses and brasses with high zinc content. Corrosion fatigue is a type of stress cracking caused by repeated cyclic stress such as tapping, shaking or vibration resulting in work hardened regions which become anodic. *Season cracking* is the term given to stress corrosion of brasses such as alpha brass, which undergo intergranular cracking under high stress in an atmosphere containing traces of ammonia or amines. The grain boundaries become anodic with respect to the grains themselves and undergo corrosion resulting in intergranular cracking. Stress corrosion is also due to the combined effects of tensile stress and corrosive environment. *Caustic embrittlement* (Sec. 14.6.4) is a form of stress corrosion encountered in mild steel steam boilers exposed to high temperatures and an alkaline medium.

13.8 Microbiological Corrosion

Aerobic organisms consume oxygen in the surrounding soil or medium thereby facilitating the differential aeration corrosion. Sulphur metabolizing bacteria (e.g., thiobacillus) convert sulphur into sulphuric acid which attacks the metals. Anaerobic sulphate reducing bacteria (*Vibrio de sulphuricans*) cause biological corrosion of iron. The corrosion products of ferrous sulphide and ferrous hydroxide are incapable of protecting iron from further corrosion and severe localised corrosion occurs. Iron and manganese metabolizing bacteria metabolize the metals into insoluble metal hydrates or oxides leading to corrosion. Film forming organisms form films on the metal surface creating concentration gradients in dissolved salts and gases which in turn facilitates corrosion. Microbiological corrosion may be avoided by proper selection of sites such as well aerated soil and avoiding clayey or water-logged locations. A protective coating of bituminous material is also helpful in inhibiting corrosion.

13.9 Intergranular Corrosion

The solidification of a molten metal or alloy starts with randomly distributed nuclei which grow into regular atomic arrays called grains. The arrangement of atoms within the grains is identical but because of random nucleation the grains have different orientations and do not match with neighbouring grains. The regions between the grains called the grain boundaries become anodic with respect to grain centers and are generally more susceptible to corrosive action by specific chemical reagents. For example chromium carbide is precipitated at the grain boundaries during welding of stainless steel and the adjacent regions are depleted in chromium concentration and become anodic and prone to corrosion. Intergranular corrosion occurs along the grain boundaries causes sudden failure of the material as it difficult to detect. Use of low carbon steels for welding can minimise this type of corrosion. Proper heat treatment followed by quenching to prevent precipitation also minimises this type of corrosion.

13.10 Erosion Corrosion

This type of corrosion is due to the turbulent flow of corroding gases and liquids as well their abrading action which breaks down the protective film on the metal surface as seen in impellers, agitators and at bends and elbows of pipes carrying fluids. Cavitation and fretting corrosion also belong to this type of corrosion. Cavitation occurs due to the formation and collapse of vapour bubbles on the metal surface resulting in a high pressure region leading to the deformation of the metal or the destruction of the protective film. Fretting corrosion occurs due to the damage of the protective film by the heat of friction and mechanical abrasion as metals slide over each other.

13.11 Stray-Current Corrosion

This type of corrosion occurs when the electric current from electric traction systems leaks into adjacent conducting structures. The point at which the current leaves the structure is anodic becoming the seat of corrosion and leads to pitting and severe damage to underground structures.

Relative sizes of catodic and anodic regions The rate of corrosion is more with the combination of a large cathodic region and a small anodic region because the greater demand for electrons at the larger cathodic region has to be met by the smaller anodic region by a greater current density at the smaller anode.

Nature of the oxide film The 'specific volume ratio', or the ratio of the volumes of the oxide film to the metal can be used to determine whether the oxide film formed on the metal will protect the metal against corrosion or not. Passivity is due to the formation of oxide films on metals such as iron, chromium, etc. The passive oxide films on iron formed by treatment of the surface of iron with concentrated nitric acid can be made damage resistant by alloying as in the case of stainless steel containing 18% Cr and 8 % Ni. Even when cracks are formed in the layer or film of oxide they heal readily making the alloy highly corrosion resistance. Other examples of corrosion resistant alloys are silicon containing cast iron and silicon containing molybdenum.

Solubility and volatility of the corrosion products If the corrosion product formed is insoluble in the surrounding medium it affords a greater corrosion resistance to the metal. Sometimes, the metal undergoing corrosion may form an insoluble product by reacting with the medium which protects the metal against further corrosion as in the case of lead forming insoluble lead sulphate in the presence of sulphuric acid. On the other hand, if the corrosion product is volatile the metal is subjected to further corrosion as seen in the case of molybdenum undergoing corrosion as the oxide MoO_3 is volatile.

13.12.2 Environment surrounding the metal

Environmental factors also influence the rate and extent of corrosion. The most important environmental factor is the differences in oxygen concentration on the surface setting up a galvanic cell (oxygen concentration cell). Other environmental factors influencing the rate and extent of corrosion include pH, humidity and presence of corrosive impurities in the atmosphere, stray electric current, nature of ions present in the surrounding medium and electrical conductivity of the surrounding medium, temperature and operating conditions to which the metal is subjected.

Setting up of an oxygen concentration cell As already discussed, differential aeration corrosion, is due to the setting up of an oxygen concentration (galvanic) cell.

Effect of pH: The pH of the surrounding medium has a decisive role in influencing the rate of corrosion as well as in corrosion control. In general, acidic media are more corrosive compared to neutral or mildly alkaline media. Amphoteric metals such as aluminum, zinc and lead undergo corrosion in both acids and alkalis. The combined effect of the oxidation potential of the metal and pH of the medium has a profound influence on the rate of corrosion.

Humidity and presence of corrosive impurities in the atmosphere Humidity of the air surrounding the metal influences corrosion, the greater the humidity higher being the rate of corrosion. Critical humidity is the humidity of the air above which the rate of atmospheric corrosion of the metal increases sharply and depends on the nature of the metal and the nature of the corrosion products. Oxide films absorb moisture in humid conditions resulting in enhanced rate of corrosion. The presence of corrosive pollutants in the atmosphere such as hydrogen sulphide, sulphur dioxide, hydrogen chloride, ammonia, chlorine, etc., particularly in industrial areas increase the rate of corrosion of metals as they provide an acidic environment as well as a medium with greater electrical conductivity.

passivation occur. Iron in contact with aqueous medium at neutral pH (pH = 7) indicated by the point X in the Figure 13.6 is susceptible to corrosion but can be protected by (i) increasing the pH of the aqueous medium to alkaline pH, (ii) by changing the potential to about –0.8 V through an external circuit (cathodic protection), or (iii) by applying a potential of opposite sign to move into the region of passivity (anodic protection).

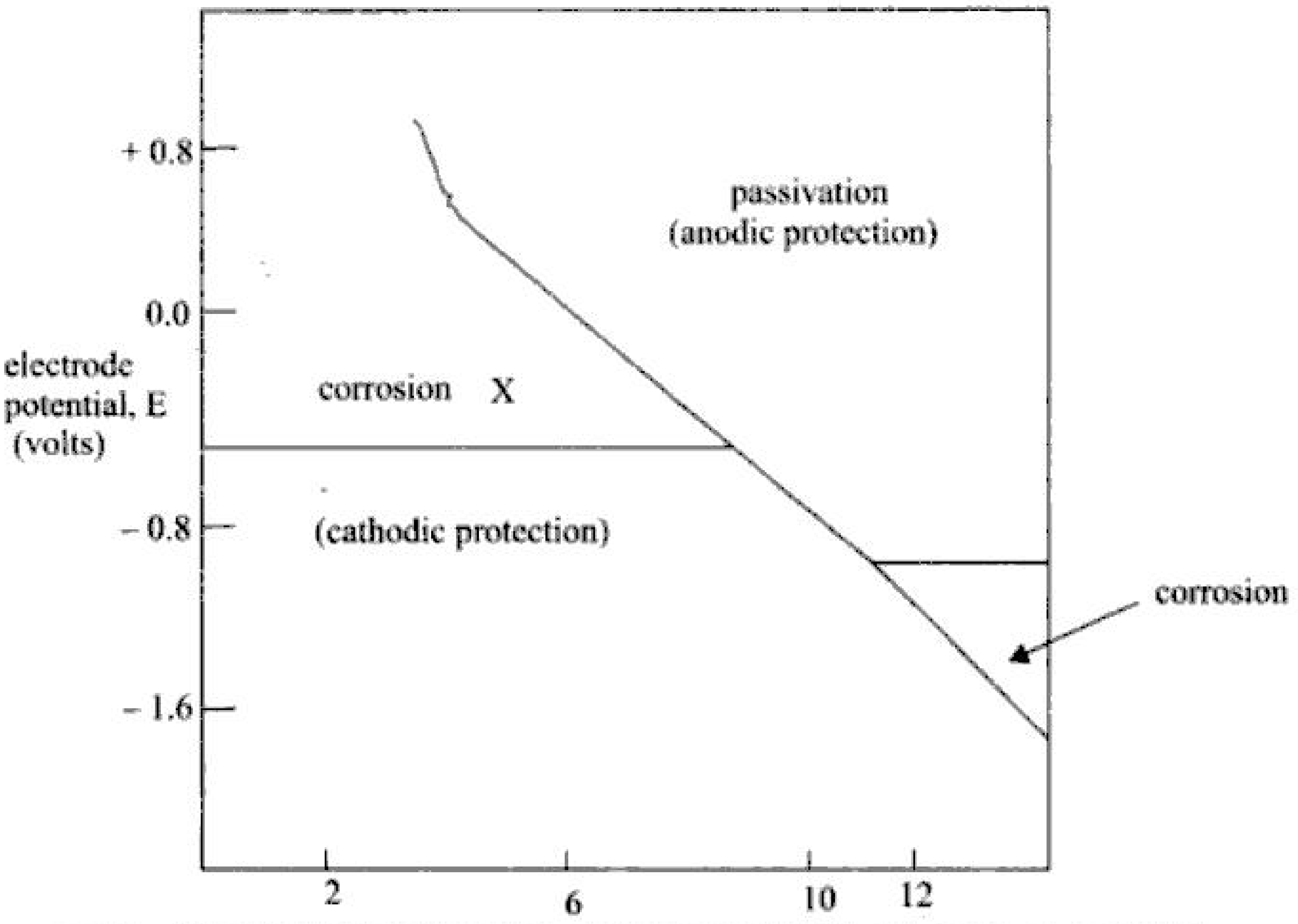


Fig. 13.6 Pourbaix diagram of an iron-water system at 25° C

The selection of metals must be such that differential metal corrosion is avoided. Pure metals are much less susceptible to corrosion. In the case of pure metals such as aluminum the oxide film formed is coherent and impervious and protects the metal against corrosion. However use of pure metals may not be possible due to their inadequate mechanical properties of strength and hardness. Further dry corrosion or corrosion by direct chemical attack cannot be prevented.

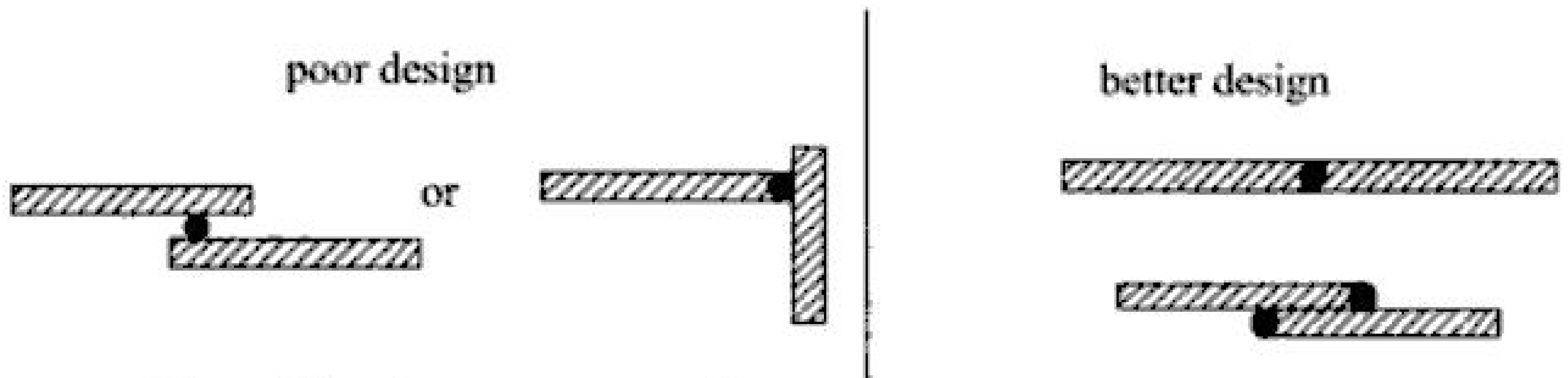
When different metals have to be used the metals closer to each other in the electrochemical series should be preferred and as far as possible, direct contact between different metals and contact with electrolytes should be avoided. An insulator incapable of any moisture absorption should be used between the metals. Since the rate of corrosion depends on the relative sizes of the anode and cathode the combination of a small anode and a large cathode should be avoided. Screws, bolts and nuts and welding material should be made from a more noble metal or alloys than the joined metals. Anti-corrosion paint may minimise the galvanic corrosion as long the protective film is not ruptured.

13.14.2 Design aspects

The principle of better design aims at preventing corrosion and even if corrosion occurs, it is not restricted to intense localised corrosion but occurs uniformly over the entire structure. The various aspects of proper designing of structures may be summarised as follows:

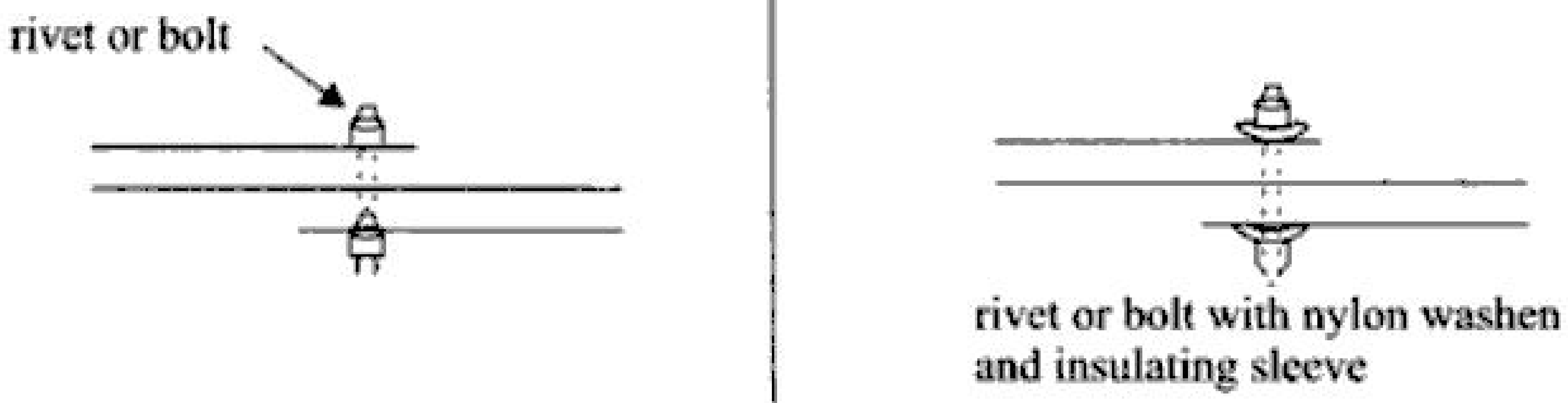
(i) The design of the structure should be such that absorption and retention of moisture is as low as possible to minimise corrosion.

(ii) The design should minimise the number of angles, corners, edges, crevices and internal surfaces (as in L, T and U shaped structures) if they cannot be avoided (Figure 13.7).



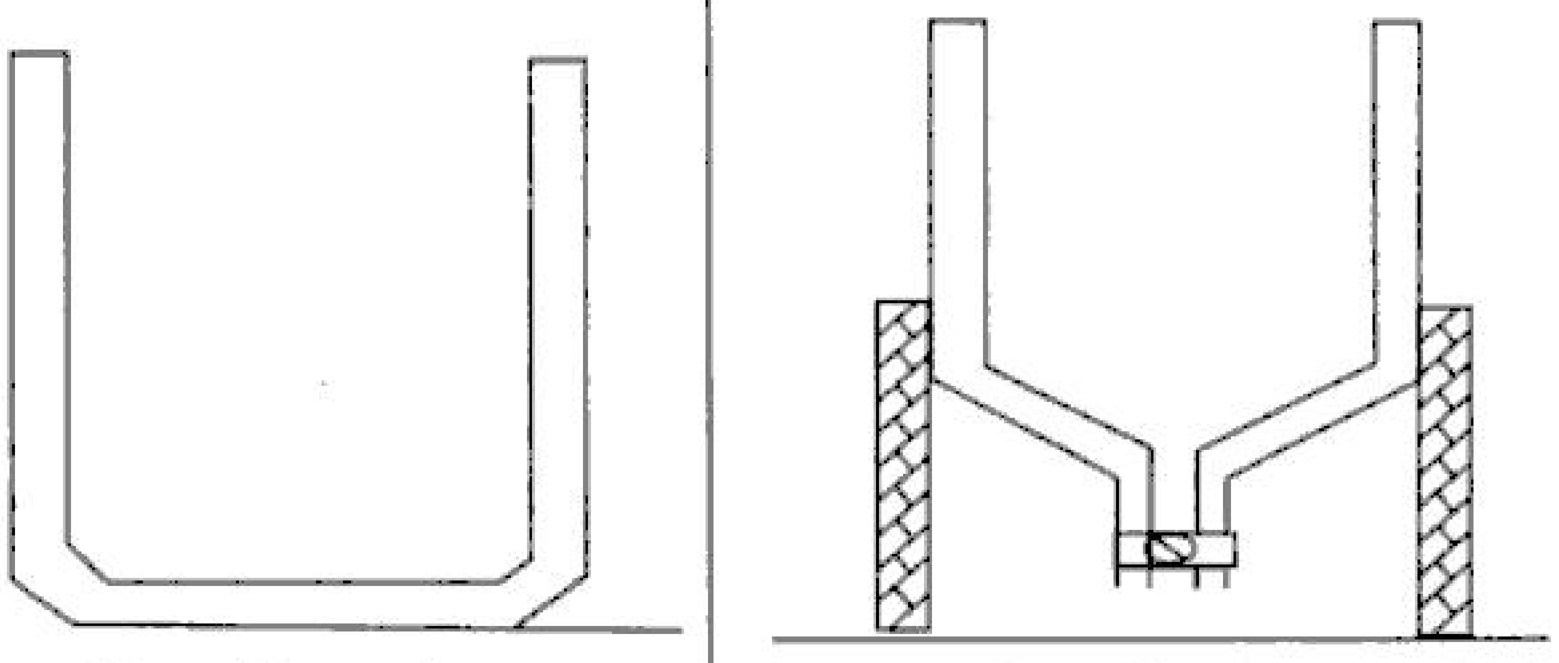
(a) avoiding sharp corners, crevices and protruding parts

proper welding



(b) avoiding galvanic corrosion

by proper insulation



(c) avoiding crevices

and providing better aeration in storage tanks

Fig. 13.7 Design aspects in the control of corrosion

(iii) The design should also take care that water does not condense and collect over the top of structures. Storage tanks should be designed to facilitate draining and cleaning of the tanks. Such structures should be supported on pillars to facilitate free circulation of air and prevent formation of stagnant pools of water or damp areas.

(iv) Continuous welds are better compared to intermittent welds both from mechanical and corrosion points of view. It is preferable that the smaller side of the weld faces the corrosive medium.

(v) The design should ensure turbulent-free flow of fluids and stress-free conditions.

Modification of properties of the metal is also achieved by refining to lower the content of corrosive elements as exemplified by the removal of carbon, sulphur and phosphorous in stainless steels. Annealing by way of heat treatment to remove residual stress in metals and bring about changes in the structure of alloys also increases corrosion resistance.

(iii) Electrochemical protection

This is especially suited for structures immersed or buried in electrically conducting liquids and soils. Two methods are usually practiced: (a) sacrificial anode method and (b) electrolytic method. In sacrificial anode method the specimen made of steel to be protected (e.g., a submerged or buried pipe or structure) is made to act as a cathode of a galvanic cell by short-circuiting it with a less noble metal such as magnesium, aluminum or zinc (sacrificial anode) as shown in the Figure 13.8. in conjunction with other protective measures such as coating to prevent corrosion at any gaps in coatings.

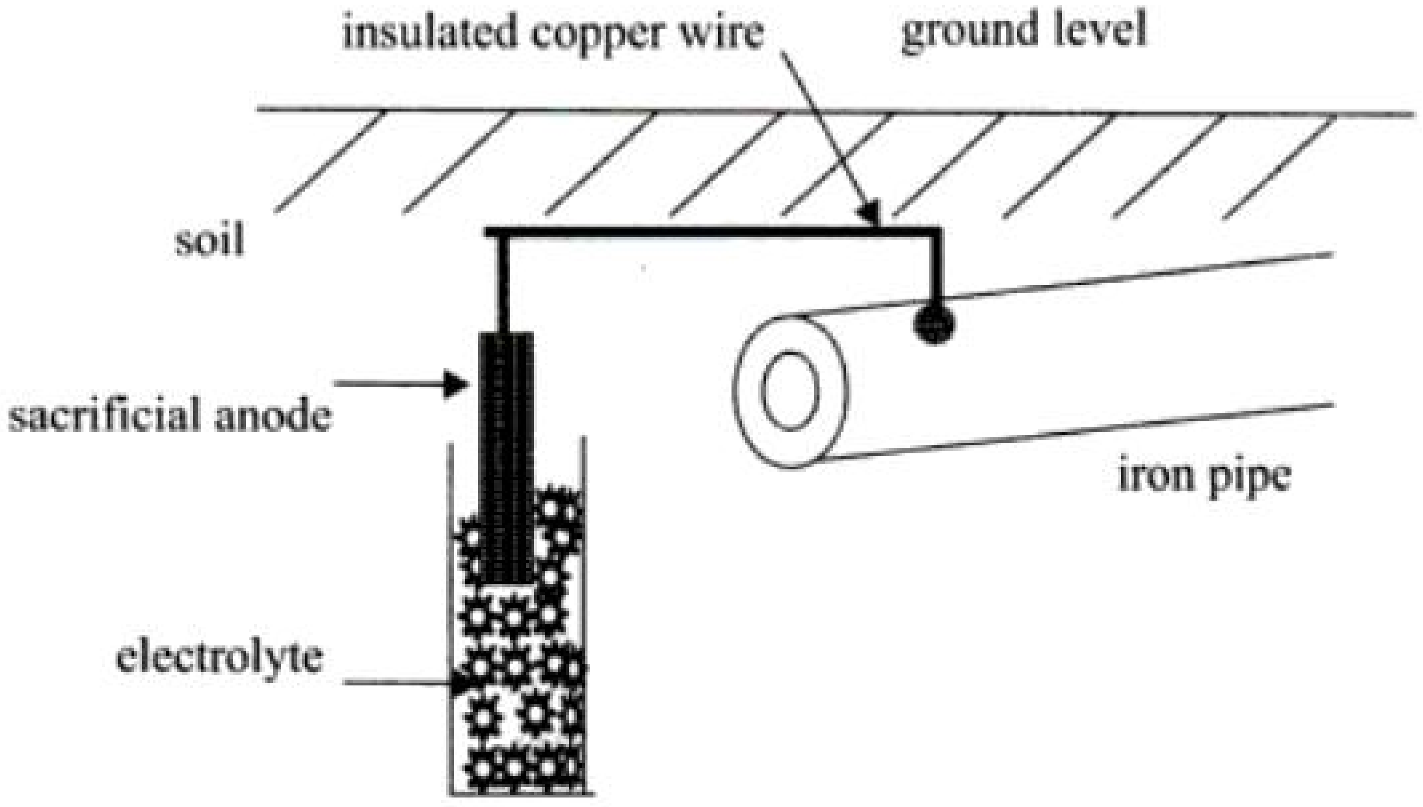


Fig. 13.8 Sacrificial anodic protection

In the electrolytic method or impressed current cathodic protection method, the object to be protected is made the cathode of an electrolytic cell by connecting it to the negative terminal of a DC source. The positive terminal of the DC source is connected to scrap iron, platinum, graphite, nickel or lead anode (insoluble anode) and buried or immersed in a conducting medium adjacent to the metal to be protected (Figure 13.9). The impressed current nullifies the corrosion current. Cathodic protection is usually adopted to protect buried structures, pipes, tanks, etc.

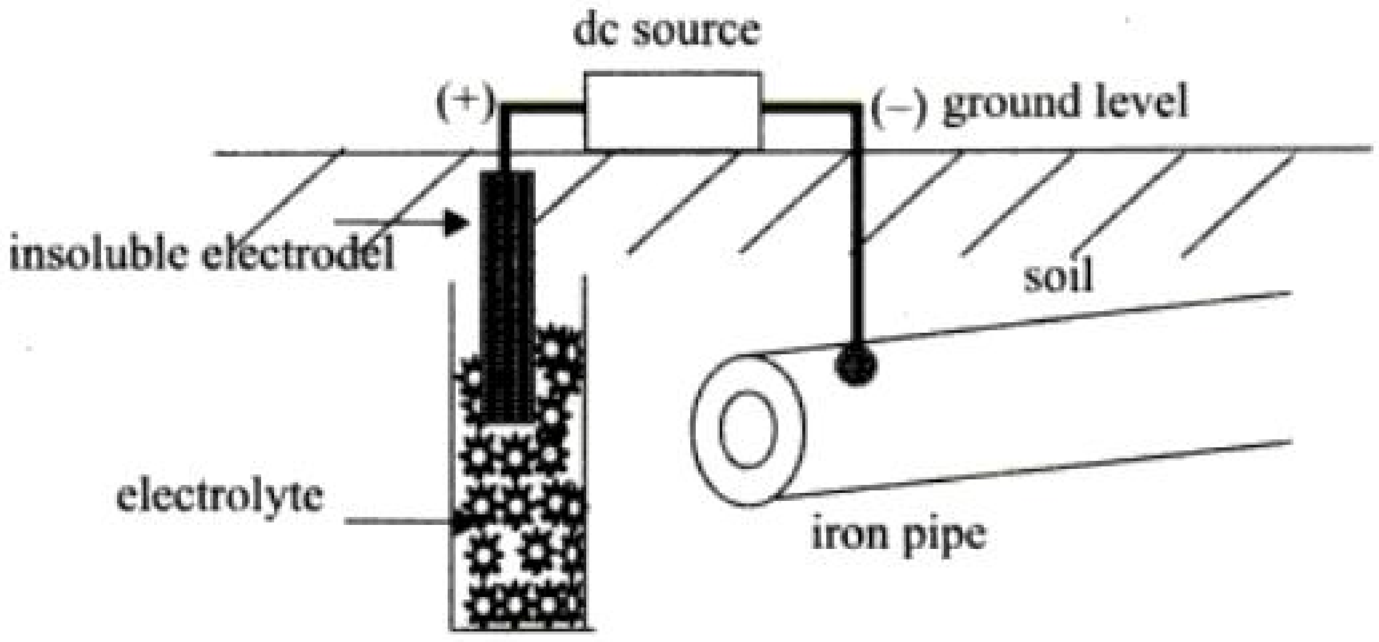


Fig. 13.9 Impressed current cathodic protection

(iv) Use of protective coatings

Corrosion always begins at the surface of a metal. Hence corrosion may be inhibited by coating the surface of the metal with metallic or non-metallic coatings. Metals such as zinc and chromium protect iron against corrosion by becoming the anode of a galvanic cell and such coatings are called anodic coatings. In contrast metals such as cadmium, nickel or tin are cathodic to iron and hence their coatings are called cathodic coatings. These metals form protective oxides preventing air and moisture from contacting the metal to be protected. However, if the oxide film is ruptured in the case of cathodic coatings, the base metal is exposed to corrosion. Non-metallic coatings include phosphate coating, chromate coating, anodising, ceramic coating (vitreous or porcelain enamel), cermets or ceramal (mixtures of ceramics and metals). Organic coatings such as pitch, tar, bitumen, oils and grease are used as temporary protective coatings against corrosion. Such coatings exclude any corrosion stimulant coming into contact with the metal to be protected. Paints, varnishes and lacquers are the most widely used organic coatings both for protection against corrosion as well as for decorative purposes.

13.15 Protective Coatings

Protective coatings are usually inert to the environment and protect the metal when applied as a thick layer on the surface of the metal. The different protective coatings currently in vogue may broadly be classified into (i) inorganic coatings consisting of metallic as well as non-metallic coatings and (ii) organic coatings.

13.15.1 Pretreatment of the surface to be protected

The surface to be protected against corrosion has to be cleaned and pretreated properly to ensure good adhesion of the coating. The major steps involved in cleaning and pretreatment of metallic surfaces include (i) degreasing, and (ii) descaling

Degreasing to remove any oil, grease or fatty substances applied on the surface as a temporary protective measure during storage is effected by solvent cleaning followed by alkali cleaning. Organic solvents such as acetone, toluene, xylene, naphtha, trichloro ethylene or tetrachloroethylene are used for degreasing the metallic surface. Solvent cleaning is followed by steaming the surface and washing with hot water containing wetting agents such as soap or synthetic detergents and alkaline cleaning reagent such as a solution of sodium phosphate or caustic soda. Alkali cleaning removes any old paint as well as any firmly held oily substances. Alkali cleaning is followed by thorough washing with water to remove any traces of alkali. The article is then immersed in an aqueous solution of sodium or potassium chromate which functions as anodic inhibitor of corrosion and affords a temporary protection till further protective coating is applied.

Descaling to remove corrosion products such as oxide scale formed on the surface is effected by any one or more methods such as mechanical methods, shot-blasting or sand blasting, flaming, or pickling depending the requirement. *Mechanical methods* of descaling use tools such as wire-brush, dull chisel, knife scraper or cutter to remove any loosely held rust and other impurities. *Shot-blasting* is adopted to remove strongly adherent scales and to give a roughened surface particularly on large steel surface, in which abrasive particles such as sand, steel grit or fused bauxite are blown onto the surface at high velocity by a stream of compressed air (pneumatic blasting). However, shot-blasting causes irritation to the respiratory tract and other associated health problems to operating personnel and hence protective measures are necessary. The shot-blasted surface is highly amenable for painting.

suspended in an electroplating bath containing the metal ions to be plated by electrodeposition. The metal to be deposited is made the anode or the anode may be an inert material with good electrical conductivity such as graphite. A variety of conditions such as the bath composition, temperature, pH, voltage, current density and agitation are optimised so that the rate of dissolution of the anode and the rate of deposition of the metal on the cathode (base metal article) are almost equal and the composition of the electrolyte bath remains unaltered. An electrolyte bath with a better 'throwing power' gives a coating of uniform thickness. Chromium plating is usually adopted to protect iron. However, the plated chromium metal is brittle and hence cracks and peels off. Therefore iron is first plated with copper, then with nickel and finally with chromium. Copper gives good adhesion, nickel affords protection and chromium enhances the appearance. The composite coating is hard and highly resistant to corrosion.

Electroless plating also known as *immersion plating* or *displacement plating* involves immersing the base metal article in a bath of a noble metal salt used for coating. The noble metal ion is displaced from the salt solution by the base metal ion and forms a thin but uniform deposit on the base metal article. For example, in electroless nickel plating, the base metal article to be plated is immersed in a bath of nickel sulphate and sodium hypophosphite at pH 4.5-5.0 and a temperature of about 100° C. The hypophosphite reduces the nickel ion to metallic nickel and finally to nickel phosphide. An alloy of nickel and nickel phosphide is deposited on the base metal article surface providing a strongly adherent non-porous coating with high corrosion resistance.

13.17 Non-Metallic Inorganic Coatings

Non-metallic inorganic coatings may be classified into two types (i) surface or chemical conversion coatings and (ii) ceramic coatings. *Surface coatings* are formed on the surface of the base metal to be protected by the deposition of less reactive and corrosion resistant compounds by chemical or electrochemical reactions. Such coatings remain an integral part of the base metal. The conversion coatings are applicable to iron and steel, aluminum and its alloys and zinc and its alloys. These coatings protect the base metal against corrosion and in addition provide an ideal surface for painting. The different types of conversion coatings commonly used include phosphate coating, chromate coating, chemical oxide coating and anodised coating.

13.17.1 Phosphate coating

This type of coating is produced by the chemical reaction between the base metal iron and the phosphating solution consisting of zinc primary phosphate, $Zn(H_2PO_4)_2$ and phosphoric acid. The reaction may be represented as

$$3\,Zn(H_2PO_4)_2 + \underset{\text{base metal}}{Fe} + 4\,H_2O \longrightarrow \underset{\text{coating}}{Zn_3(PO_4)_2.\,4\,H_2O} + FeHPO_4 + 3\,H_3PO_4 + H_2 \qquad (13.15)$$

The hydrogen formed in the above reaction collects as bubbles or a film on the surface of iron slowing down the rate of phosphate coating. Hence accelerators such as nitrates, nitrites or chlorates are added to the phosphating solution to oxidize the hydrogen to water thereby enhancing the rate of coating.

The phosphating solution is applied on mechanically cleaned iron or steel surface by dipping, spraying, brushing or swabbing. The grey coloured phosphate coating is not corrosion resistant but provides a good base for painting or impregnation with oils. Iron and manganese phosphate coating is used in piston rings, cylinder lining of automobiles and wire drawing equipment to reduce wear due to friction.

paint is usually painted over the anti-corrosive primer particularly for ship's bottom mainly to prevent the growth of aquatic organisms such as fungi, barnacles and tubeworms. Anti-fouling paints contain components such as copper oxide, mercuric oxide and organomercury compounds which are toxic to aquatic organisms along with binders such as vinyl resins, phenolic resins or chlorinated rubber.

Thixotropic paints Thixotropy is a property exhibited by a suspension which on stirring or agitation attains the consistency of a liquid (sol) and if left undisturbed for some time sets to a gel-like consistency. The gel-sol transition is reversible. Thixotropic paints incorporate extenders such as china clay or metal soaps of aluminum, calcium and zinc or a thixotropic vehicle such as alkyds treated with polyamines (e.g., ethylene diamine) at higher temperatures. These paints find use in the painting of ceilings or for applying a thick coat of paint without the associated problems of dripping from brush, running or sagging on the painted surface.

13.20 Defects in Paint Films

Paint films develop a variety of defects over the course of time. It is necessary to understand the nature of defects and their causes in order to enhance the durability of paint films. The types of defects commonly encountered include those that are formed (i) during application and (ii) on finished surfaces.

13.20.1 Defects formed during application of paint

Blistering Blisters appear as bubbles or hollow projections on a paint film. Blistering occurs due to painting a wet or chemically contaminated surface, painting in excessively hot conditions or applying paint as a heavy coat. Blister formation can be avoided by proper pretreatment of the surface, using a suitable primer, proper dilution with suitable solvents and applying paint in a uniform thickness.

Blushing The milky white coating on the painted surface is called blushing and is caused by painting under humid conditions or by the use of low boiling thinner. This can be avoided by painting under dry conditions and proper selection of thinner.

Cissing When the surface to be painted is not free from grease or when the paint is contaminated with silicone grease, the applied paint recedes over small areas of the painted surface due to inadequate wetting of the surface by the paint.

Lifting This occurs due to the incompatibility between the primer or first coat of paint and the paint used for top coat. If the first coat of paint dries slowly compared to the top coat paint, the first coat becomes softer and lifts off the surface.

Orange peeling When the paint is applied using a spray gun, the paint may not level out properly resulting in pock-marked appearance just like the outer surface of an orange peel. This is avoided by proper adjustment of flow properties with a suitable thinner and spray painting the surface as a thin and uniform coat.

Pin holing The use of a viscous paint or improper mixing of the paint and the thinner results in the formation tiny circular holes with solid deposit at the centre.

Wrinkling The use of excessive amount of drier in the paint and application of paint as a heavy coat or under excessive heat produces wrinkles of the painted surface. This can be avoided by controlling the proportion of drier and use of suitable thinner.

13.20.2 Defects formed on finished surfaces

Chalking Chalking, i.e., weathering of the paint film resulting in the formation of a loose removable powder, occurs due to erosion of the binder in the paint film caused by the simultaneous attack by oxygen and light. Chalking decreases the thickness of the paint film. The use of weather resistant pigments prevents chalking.

Temporary hardness, is attributed to the presence of bicarbonate salts of calcium and magnesium. These salts are decomposed to form insoluble calcium carbonate and magnesium hydroxide by boiling the water and may be filtered off to remove temporary hardness.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2 \tag{14.2}$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2\,CO_2 \tag{14.3}$$

Permanent hardness cannot be destroyed or removed by boiling the water. It is attributed to the presence of chlorides and sulphates of primarily calcium and magnesium and to a minor extent of iron and other heavy metals.

Hardness of water used to be determined by the thickness of the lather layer formed by the test sample and 'standard' hard water under identical conditions. The semi-quantitative method has been replaced by the more reliable and easy to perform EDTA titrations.

The determination of total hardness of water by EDTA method involves the determination of the total amount of calcium and magnesium present in a given volume of water. The sample water of known volume is buffered to a pH of about 10 with ammonia-ammonium chloride buffer and titrated against a standard solution of disodium salt of ethylenediamine tetraacetic acid (EDTA) taken in the burette, in the presence of 40–50 mg of eriochrome black T (solochrome black T) as indicator. The indicator forms wine-red coloured metal ion-indicator complex with a small amount of the calcium and magnesium in the sample water. The metal ion-indicator complex is relatively less stable compared to the metal ion-EDTA complex (MY^{2-}). The added EDTA (H_2Y^{2-}) interacts with the freely available calcium and magnesium in the water forming soluble colourless complex of stoichiometry 1:1. When all the freely available calcium and magnesium is exhausted the added EDTA displaces the indicator from the metal ion-indicator complex liberating the blue coloured free indicator HIn^{2-}. Thus the colour change at the end point is red to blue in this titration.

$$M^{n+} + HIn^{2-} \longrightarrow MIn^- + 2\,H^+ \tag{14.4}$$

$$\underset{\text{(wine red)}}{MIn^-} + H_2Y^{2-} \longrightarrow \underset{\text{(blue)}}{MY^{2-} + HIn^{2-}} \tag{14.5}$$

The amount of the total hardness (amount of calcium and magnesium) is calculated on the basis of the stoichiometric relationship and is expressed in terms of equivalent amount of calcium carbonate in units of parts per million (ppm) or milligram per liter (mg/L). The stoichiometric relationships are

1000 ml of 1 M EDTA = 1g.atomic weight of metal

1 ml of 1 M EDTA = 100 mg of $CaCO_3$.

Permanent hardness is determined by a titration with a standard solution of disodium salt of EDTA after destroying the temporary hardness. Temporary hardness is destroyed by boiling the sample water to thermally decompose the bicarbonates of calcium and magnesium and precipitate calcium carbonate and magnesium hydroxide. The sample water is cooled to room temperature and filtered through a Whatman No.1 filter paper to remove the precipitate. The precipitate is washed with distilled water and washings are added to the filtrate which is then buffered to pH 10 with ammonia-ammonium chloride buffer and titrated against the same standard solution of disodium salt of EDTA using eriochrome black T indicator. The permanent hardness of the sample water is the amount of calcium and magnesium determined.

Temporary or carbonate hardness of water is obtained by calculation subtracting the amount of permanent hardness from the value of total hardness. Carbonate hardness of water is also responsible for the alkalinity of water and can be estimated by neutralisation titrations.

Coagulant aids are often added to improve the efficiency of coagulation process. Commonly used coagulant aids include activated silica (prepared from the reaction between sodium silicate and hypochlorous acid) and polyelectrolytes or polymeric electrolytes. Polyelectrolytes may be non-ionic (e.g., polyacrylamide and polyethylene oxide), cationic (e.g., polydiallyldimethyl ammonium salt), anionic (e.g., polyacrylate) or ampholytic containing both cationic and anionic sites (e.g., polylysineglutamate).

The coagulants in required quantities are added in solution form to raw water and rapidly mixed by flash mixing. The water is then allowed to flow into flocculation tanks and subjected to gentle agitation by slow moving baffles to facilitate the build up of particle size and the process is called **flocculation**. After sufficient residence time the water flows into sedimentation tanks for clarification and settled solids (sludge) is scrapped off continuously or intermittently. Alternatively the coagulated water is subjected to upward flow through a previously formed sludge in tanks whose cross-sectional area increases gradually from bottom to the top. The slurry of old and newly formed floc flows upward and as the velocity of the upward moving water decreases with height the particles settle to form a floating sludge blanket. The rising water flows through the floating sludge blanket which serves as a filter bed to remove suspended particles (*sludge-blanket filtration*). The clarified water flows out from the top.

Filtration aims at complete removal of suspended particles, colloidal matter as well as microorganisms by passing water through a porous medium capable of retaining the coarse particle on the surface and the finer impurities in the pores. The filter medium is usually a sand filter consisting of four different layers. The layers from the top consist of fine sand placed over the next layer of coarse sand followed by a third layer of fine gravel placed over the last layer of coarse gravel as shown in the Figure 14.1.

Water from sedimentation tanks is distributed uniformly over the entire fine sand bed and allowed to flow by gravity through the different layers. Filtration is stopped when the rate of filtration decreases largely due to the accumulation of sediments on the filter bed. The sand bed filter medium is scrapped off and the entire filter medium is relayed with fresh sand bed. Rapid gravity filtration uses carefully graded quartz sand as the filter medium. It has the advantages of enhanced rate of filtration and quick cleaning of the filter medium by compressed air agitation followed by back flushing with clean water to wash off the accumulated impurities.

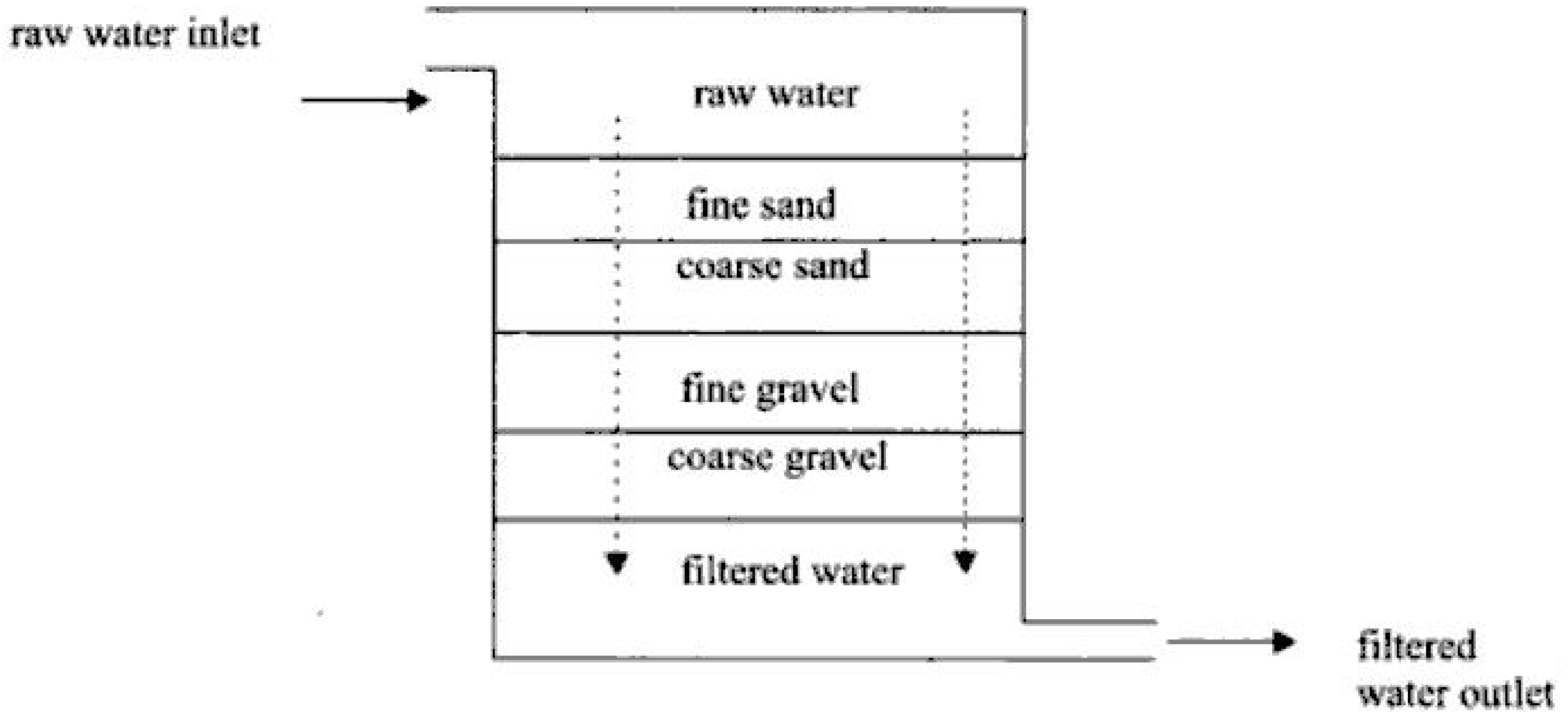


Fig. 14.1 Schematic diagram of a filter unit consisting of layers of sand and gravel

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mixing occurs and softening of water takes place. The sludge settles down at the bottom while the softened water moves upward into the outer chamber, passes through a filter medium of wood fiber to ensure the complete removal of any residual sludge particles and finally the clarified water flows out through the outlet at the top of the vessel. The sludge is removed from the bottom of the tank periodically.

The coagulant used in the cold lime-soda process also requires lime and soda in addition to the hardness causing constituents of water as per the equations given below:

$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2 + Ca^{2+} + SO_4^{2-} \tag{14.29}$$

$$Al_2(SO_4)_3 + 3\,Ca(OH)_2 \longrightarrow 2\,Al(OH)_3 + 3\,Ca^{2+} + 3\,SO_4^{2-} \tag{14.30}$$

Sodium aluminate undergoes hydrolysis due to increase in the hydroxide concentration by the added lime to precipitate aluminum hydroxide and generate sodium hydroxide as per the equation

$$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + Na^+ + OH^- \tag{14.31}$$

The cold lime-soda process usually brings down the hardness to a residual value of 50–60 ppm. The process conditions may be varied to suit the purpose for which the softened water is required. A partial softening of raw water leaving a residual hardness in the range 80–90 ppm is adopted for drinking water as too soft a water will lead to plumbosolvency or solubilization of lead (of pipes) in water. The solubility of lead in water is low in the presence of bicarbonate ions, the larger the concentration of bicarbonate, lower the solubility of lead in water. The cold lime-soda process is more effective for the removal of carbonate (or temporary) hardness. For efficient softening of water particularly the boiler feed water cold lime-soda process is combined with other methods of water softening such as zeolite or ion-exchange process which are effective and economical for the removal of permanent hardness.

Hot lime-soda process involves softening of water by lime and soda at temperatures close to the boiling temperature of water. The chemical reactions proceed at a faster rate and since the viscosity of water is low at higher temperatures and precipitates sludge settle down easily eliminating the addition of coagulants. An additional advantage is that dissolved gases such as oxygen, carbon dioxide and air are expelled. In practice the raw water along with chemicals is sprayed into superheated steam and mixed thoroughly in a reaction tank as shown in the Figure 14.4. The mixture then passes into a conical sedimentation tank to allow the sludge to settle down. The softened water is then passed through a sand filter or a sludge blanket to filter off any residual sludge particles. Hot lime-soda process is almost exclusively used for softening boiler feed water. The softened water may be passed through a filter bed containing graded anthracite coal or a phosphate treatment plant to achieve near zero hardness before being pumped into the boiler.

Lime-soda process has many advantages in that it increases the pH of the softened water thereby reducing corrosion of feed and distribution pipes and the process is economical. The microbial load particularly that of pathogenic organisms, is considerably reduced in the softened water. Disadvantages include inability to soften water to less than 15–20 ppm, generation of a large amount of sludge and its disposal. The process also requires well trained and skilled operators.

$$2\ Fe + H_2O + O_2 \longrightarrow 2\ Fe(OH)_2 \qquad (14.36)$$

$$4\ Fe(OH)_2 + O_2 \longrightarrow 2\ Fe_2O_3.2\ H_2O\ \text{(rust)} \qquad (14.37)$$

Dissolved oxygen is removed by adding a calculated quantity of reducing agents such as sodium sulphite, sodium sulphide or hydrazine.

$$2\ Na_2SO_3 + O_2 \longrightarrow 2\ Na_2SO_4 \qquad (14.38)$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4 \qquad (14.39)$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2\ H_2O \qquad (14.40)$$

14.6.4 Caustic embrittlement

This is caused by the highly alkaline nature of water in the boiler. A small amount of residual sodium carbonate present in the lime-soda softened water decomposes at higher temperatures and pressures to give sodium hydroxide and carbon dioxide rendering the water caustic.

$$Na_2CO_3 + H_2O \longrightarrow 2\ NaOH + CO_2 \qquad (14.41)$$

The dissolved sodium hydroxide flows into minute cracks in the inner side of the boiler by capillary action. Over a period of time the concentration of sodium hydroxide increases resulting in the dissolution of the iron of the boiler. A concentration cell is also formed due to differences in the concentration of sodium hydroxide in the different parts of the boiler. The region of the boiler surrounded by dilute sodium hydroxide acts as a cathode while the region surround by concentrated sodium hydroxide acts as the anode and anodic region undergoes corrosion. This caustic embrittlement of boiler parts occurs particularly at stressed parts like bends and joints ultimately leading to boiler failure. Caustic embrittlement is avoided by using sodium phosphate as a softening agent instead of sodium carbonate and by adding certain chemicals such as lignin, tannin or sodium sulphate to boiler water which block the minute cracks thereby preventing the entry of sodium hydroxide solution.

14.7 Boiler Feed Water Treatment

Boiler feed water thus should satisfy the stringent specifications of hardness (< 0.2 ppm), caustic alkalinity (0.15–0.45 ppm), soda alkalinity (0.15–1.0 ppm) and soda ash (0.3–0.55 ppm). In order to satisfy the specifications boiler feed water in treated in two stages (i) ***external treatment***, and (ii) ***internal treatment***.

14.7.1 External treatment of boiler feed water

The treatment involves the removal of scale and sludge forming substances and corrosion causing substances by (i) softening of water to remove hardness or scale forming salts, (ii) removal of silica, and (iii) removal of suspended matter, (iv) removal of dissolved gases such as oxygen and carbon dioxide, and (v) removal of oil.

Water softening to remove the hardness causing species is carried out by any of the following methods (a) lime-soda process, (b) zeolite process, (c) ion-exchange process, and (d) distillation. Demineralization by ion exchange method is the only method to decrease the hardness to a desired level for boiler feed water particularly for high pressure boilers.

Silica is removed by chemical treatment with magnesium oxide or dolomitic lime to precipitate magnesium silicate or by the addition of ferric sulphate and sodium hydroxide as coagulants for

Convert the individual concentrations to $CaCO_3$ equivalents.

100 ppm of Ca^{2+} = (100/40) × 100
= 250 ppm of $CaCO_3$

42 ppm of Mg^{2+} = (100/24) × 42
= 175 ppm of $CaCO_3$

60 ppm of CO_2 = (100/44) × 60
= 136 ppm of $CaCO_3$

21 ppm of HCO_3^- = (100/122) × 212
= 173.8 ppm of $CaCO_3$

5 ppm of H^+ = (100/2) × 5
= 250 ppm of $CaCO_3$

8 ppm of $NaAlO_2$ = (100/164) × 8
= 4.88 ppm of $CaCO_3$

25 ppm of CO_3^{2-} = (100/60) × 25
= 41.7 ppm of $CaCO_3$

15 ppm of OH^- = (100/34) × 15
= 44.1 ppm of $CaCO_3$

CaO requirement = (56/100) × [Mg^{2+} + CO_2 + HCO_3^- + H^+ + OH^- – $NaAlO_2$]
= (56/100) × [175 + 136 + 173.8 + 250 + 44.1 – 4.88]
= (56/100) × 774.02 = 433.45 mg/l

For 50,000 liters of water
= 433.45 mg/l × 50,000 l × (1/1000) = 21,672.56 g
or **21.672 kg of CaO**

Na_2CO_3 requirement = (106/100) × [Ca^{2+} + Mg^{2+} + CO_3^{2-} + OH^- – HCO_3^- – H^+]
= (106/100) × [250 + 175 + 41.7 + 44.1 – 173.8 – 250]
= (106/100) × 87 = 92.22 mg/l

For 50, 000 liters of water = 92.22 mg/l × 50,000 l × (1/1000)
= 4611 g or **4.611 kg of Na_2CO_3**

◆

7. A zeolite bed was exhausted after removing completely the total hardness of 20,000 liters of water. It required regeneration with 150 liters of a solution containing 100 g/l of NaCl. Calculate the hardness of water.

Solution:

NaCl present in 150 liters of regenerating solution
= 150 l × 100 g/l = 150,000 g

$CaCO_3$ equivalents of 150,000 g of NaCl
= (50 g eq. of $CaCO_3$/58.5 g eq. of NaCl)
= 12820.5 g

The total hardness removed by the zeolite bed in 20,000 liters of water = 12820.5 g

Therefore the total hardness in terms of $CaCO_3$
= 12820.5/20,000 = 0.641 g or **641 mg/l**

◆

Review Questions

1. What are the different types of impurities associated with water?
2. What is hardness of water due to? How is it expressed?
3. How are total, permanent and temporary hardness of water determined?
4. How is calcium hardness of water determined?
5. How is the different types of alkalinity of water identified and quantitatively analysed?
6. How is dissolved oxygen content of water determined?
7. Give a detailed account on the various stages involved in the treatment of water for drinking purpose.
8. Explain the term break-point chlorination?
9. Detail the methods used for the disinfection of drinking water.
10. What are coagulants and floccculants? How do they function?
11. Discuss in detail the principle and practice of lime-soda process.
12. Describe the hot lime soda process and list its advantages.
13. Write a note on water softening by zeolite process. List the advantages and disadvantages of the process.
14. What is demineralization? How is it carried out?
15. Give a detailed account on boiler troubles.
16. Explain the terms caustic embrittlement, priming and foaming.
17. Write a note on internal treatment of boiler water.
18. Give a detailed note on the external treatment methods adopted for treating boiler feed water.
19. What is the effect of dissolved oxygen in boiler feed water? How is dissolved oxygen removed?
20. What is desalination sea water ? How is it achieved?
21. Discuss the principle involved in the operation of reverse osmosis and electrodialysis.
22. Explain the term Langelier index and its significance.

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to carbon dioxide and nitrogen by using powerful oxidizing agents such as chlorine, hypochlorite or hydrogen peroxide in the presence of a copper salt as catalyst.

$$2\,CN^- + 5\,Cl_2 + 8\,OH^- \longrightarrow 2\,CO_2 + N_2 + 10\,Cl^- + 4\,H_2O \qquad (15.15)$$

15.11 Modern Wastewater Treatment Techniques

In the last few years a variety of high tech methods have been developed and put into practice for the purification of wastewater particularly to remove dissolved pollutants such as chloro-organics, phenols, cyanides and heavy metals. The methods include (i) destruction of volatile organic compounds (ii) advanced oxidation methods and (iii) photocatalytic process.

15.11.1 Destruction of volatile organic compounds (VOCs)

Volatile organic compounds consisting of organic solvents and other chemicals are removed from wastewater by *air stripping* or *by adsorption* onto activated carbon. In ***air stripping*** air is passed upward countercurrent to the downward stream of wastewater and the volatile materials are transferred to the gas phase. However highly soluble organic compounds cannot be easily stripped. The VOCs present in the air stream are destroyed by *catalytic oxidation*. The humid air containing the VOCs is passed over precious metal catalyst supported over alumina at temperatures in the range of 300–500° C to oxidize the carbon to carbon dioxide and hydrogen to water vapour. Any chlorine present in the form of chlorinated organics in the VOCs will yield HCl in the air stream. The acid vapours have to be removed by scrubbing the air stream with lime or a basic substance before exhaust air is released to atmosphere. ***Adsorption*** onto activated carbon or other synthetic carbonaceous adsorbents is a cost-effective methodology to remove nonvolatile as well as low concentrations of volatile organic compounds. The exhausted adsorbents may be regenerated by thermal treatment or treatment with solvents and the concentrated pollutants may be destroyed by catalytic oxidation.

15.11.2 Advanced oxidation methods or processes (AOMs or AOPs)

These methods aim at complete *mineralization* of organic pollutants including those organic substances which are resistant to conventional methods of treatment by oxidizing them to carbon dioxide, water and mineral acids such as HCl. The AOMs include hydrogen peroxide oxidation, uv irradiation in the presence of hydrogen peroxide or ozonation. In the first two methods, significant amounts of highly reactive hydroxyl free radicals (OH•) are generated by the decomposition of hydrogen peroxide either by self-decomposition or by uv irradiation. The hydroxyl radical is a powerful non-selective oxidizing agent with a high oxidation potential of about 2.8 V capable of attacking and destroying any organic molecule. However, the generation of hydroxyl radical is relatively expensive and hence the method can be used economically to treat wastewaters containing organic compounds not amenable for conventional methods of treatment. Ozone can be generated by exciting oxygen electrically in ozone generators. It is also a powerful oxidizing agent capable destroying organic molecules. Ozone also undergoes decomposition induced by uv radiation to give free oxygen atoms which are highly reactive. In addition they also react with water to generate free hydroxyl radicals.

Direct chemical oxidation of solid and liquid organic wastes in aqueous phase is yet another method useful particularly where uv light is not available. Strong oxidizing agents such as peroxydisulphate ion ($S_2O_8^{2-}$), peroxymonosulphate (HSO_3^-) and ferrate ion (FeO_4^{2-}) have been found to be effective in destroying the organic wastes.

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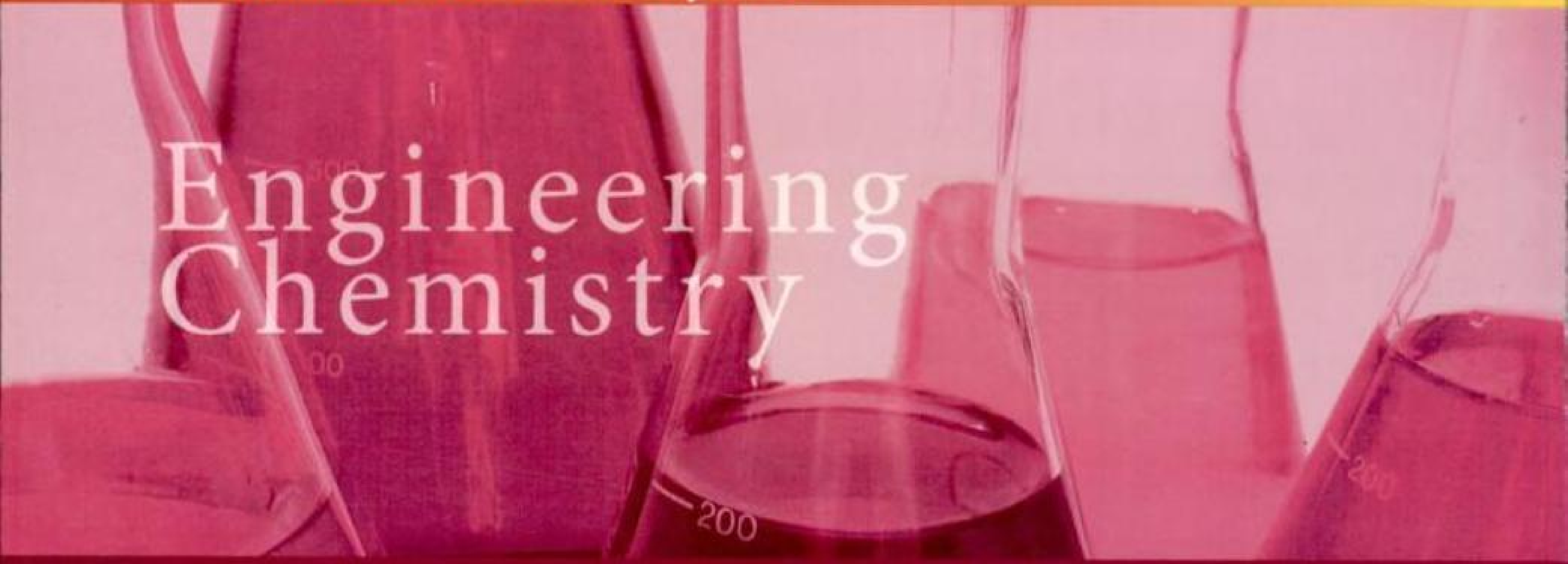

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